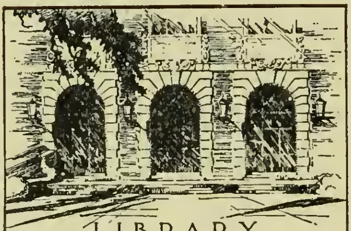

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EDITED BY

IRA REMSEN

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY

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CONTENTS VOL. XIV.

No. 1.

PAGE

ON THE ISOMORPHISM AND COMPOSITION OF THORIUM AND URANOUS SULPHATES. By W. F. Hillebrand and W. E. Melville, . . . 1

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY:

VI. *The Digestibility of the Pentose Carbohydrates.* By W. E. Stone, ... 9

CARBON DIOXIDE IN THE URINE. By T. C. Van Nüys and R. E. Lyons, ... 14

CONTRIBUTIONS FROM THE SHEFFIELD BIOLOGICAL LABORATORY OF YALE UNIVERSITY:

A Study of the Proteids of the Corn or Maize Kernel. By R. H. Chittenden and Thomas B. Osborne, ... 20

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY:

Decomposition with Alcohol of the Diazo Compounds obtained from some of the Nitro-naphthyl-amines. By W. R. Orndorff and M. Cauffman, ... 45

REVIEWS AND REPORTS.

STEREOCHEMISTRY, ... 58
THE CHEMICAL ANALYSIS OF IRON, ... 70
A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY, ... 72
A SYSTEM OF INORGANIC CHEMISTRY, ... 73

NOTES.

Free Hydroxylamine, ... 76
The Preparation of Hydrazoic Acid, ... 78
The Vapor-density of Ammonium Chloride, ... 79
Iron-carbon Oxide, ... 80

~~B1877~~

No. 2.

RESEARCHES ON THE DOUBLE HALIDES. By Ira Remsen, . . 81
- I. *On the Double Halides of Tin.* By George M. Richardson, 89
- II. *On the Double Halides of Lead.* By Charles H. Herty, . 107
- III. *On the Double Halides of Manganese.* By Charles E. Saunders, ... 127
- IV. *On the Double Halides of Antimony.* By Charles E. Saunders, ... 152
- V. *On the Double Halides of Bismuth.* By C. Pliny Brigham, 164
- VI. *Experiments with Mercurous Hypochlorsulphite.* By J. E. Gilpin, ... 182

No. 3.

THE COLORS AND ABSORPTION-SPECTRA OF THIN METALLIC FILMS AND OF INCANDESCENT VAPORS OF THE METALS; WITH SOME OBSERVATIONS ON ELECTRICAL VOLATILITY. By William L. Dudley, ... 185

THE VOLUME LAG AND ITS BEARING ON MOLECULAR CONSTITUTION. By C. Barus, ... 191

ON CITRONELLONE, AN UNSATURATED FATTY ALDEHYDE. By Edward Kremers, ... 203

PROTEIDS OR ALBUMINOIDS OF THE OAT KERNEL. Second Paper. By Thomas B. Osborne, ... 212

EUPATORIN: THE ACTIVE PRINCIPLE OF EUPATORIUM PERFOLIATUM. By C. H. Shamel, ... 224

DI-BENZYLCARBINAMINE AND ITS CONDUCT TOWARD NITROUS ACID. By W. A. Noyes, ... 225

AN IMPROVED PIPETTE FOR GAS ABSORPTIONS. By Augustus H. Gill, ... 231

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY:

XVIII.—*On the Copper Sulphites.* By Spencer B. Newbury, ... 232

REVIEWS AND REPORTS.

TAUTOMERISM, W. R. Orndorff, ... 238

OUTLINES OF THEORETICAL CHEMISTRY (Lothar Meyer), . . 246

A DICTIONARY OF CHEMISTRY (T. E. Thorpe), ... 246

HÜLFSBUCH ZUR AUSFÜHRUNG CHEMISCHER ARBEITEN FÜR CHEMIKER, PHARMACEUTEN UND MEDICINER (Hugo Schwanert), . 247

LABORATORY PRACTICE, A SERIES OF EXPERIMENTS ON THE FUNDAMENTAL PRINCIPLES OF CHEMISTRY, A COMPANION VOLUME TO THE NEW CHEMISTRY (Josiah Parsons Cooke), . . 247

METHODS OF GAS ANALYSIS (Walther Hempel), ... 248

A TEXT-BOOK OF ELEMENTARY CHEMISTRY, THEORETICAL AND INORGANIC (George F. Barker), ... 249

LEHRBUCH DER TECHNISCHEN CHEMIE (H. Ost), ... 249

HANDBUCH DER PHOTOGRAPHIE (H. W. Vogel), ... 250

MANUAL OF CHEMICAL TECHNOLOGY (Rudolph von Wagner), . 250

GRUNDLAGEN DER CHEMIE (D. Mendelejeff); THE PRINCIPLES OF CHEMISTRY (D. Mendeléeff), ... 251

NOTES.

Wolcott Gibbs Fund for Chemical Research (I. R.), 252. Stas (E. R.), 254. Hermann Kopp (W. W. R.), 257. T. Sterry Hunt (W. W. R.), 258. Wilhelm Dittmar, 259. On the Preparation of Formic Acid (Felix Lengfeld), 259. From a Letter of Dr. Wolcott Gibbs to the Editor, 260.

No. 4.

A REDETERMINATION OF THE ATOMIC WEIGHT OF CADMIUM. By H. N. Morse and H. C. Jones, ... 261

Note on Crystals of Metallic Cadmium. By George H. Williams, ... 273

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, WORCESTER, MASS.:

On the Ethers of Quinone-Oxime (Nitroso-Phenol). First Paper. By J. L. Bridge, ... 276

THE COMPOSITION OF THE EXPLOSIVE COPPER AND SILVER COMPOUNDS OF ACETYLENE. By Edward H. Keiser, ... 285

MENTHENE. By F. A. Sieker and Edward Kremers, ... 291

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY:

X. *On the Action of Acetyl Chloride on Ortho-Hydroxy-Aldehydes.* By W. P. Bradley and F. B. Dains, . 293

A NEW COLOR-STANDARD FOR NATURAL WATERS. By Allen Hazen, 300

THE CONDENSATION-PRODUCTS OF FURFUROL WITH AROMATIC BASES. By G. J. L. de Chalmot, ... 310

THE TRANSPORTATION OF SOLIDS IN A VACUUM BY THE VAPORS OF METALS. By H. N. Morse and John White, Jr., ... 314

REVIEWS AND REPORTS.

STEREOCHEMISTRY. THE STEREOCHEMISTRY OF NITROGEN (A. Eiloart) 316

NOTES.

A. W. von Hofmann (I. R.), ... 329

No. 5.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE:

LXXIII. *On the Products obtained by the Action of Nitric Acid upon Bromtrinitrophenylmalonic Ester.* By C. Loring Jackson and W. B. Bentley, . . 331

LXXIV. *Note on Tribrommononitrobenzol.* By C. Loring Jackson and W. B. Bentley, ... 363

CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN:

On the Saponification of the Substituted Acetic Esters. By Paul C. Freer and F. L. Dunlap, ... 366

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS:

I. *A Note upon the Reduction of Symmetrical Triamido-Trinitro-Benzene.* By Arthur W. Palmer, . . . 377

ON THE FORMATION OF LAYERS IN SOLUTIONS OF SALTS IN MIXTURES OF WATER AND ORGANIC LIQUIDS. By C. E. Linebarger, 380

REVIEWS AND REPORTS.

THE CONFIGURATION OF GRAPE-SUGAR AND ITS ISOMERS (W. E. Stone), ... 399

CONSTITUTION OF BENZENE (I. R.), ... 405

No. 6.

CONTRIBUTIONS FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN:

Some Reactions with Acetoacetic Ether and with Salicylic Ether. By Paul C. Freer, ... 407

THE ATOMIC WEIGHT OF PALLADIUM. By Harry F. Keller and Edgar F. Smith, ... 423

THE ELECTROLYTIC SEPARATION OF PALLADIUM AND PLATINUM FROM IRIDIUM. By Edgar F. Smith, ... 435

ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS. By H. N. Stokes, ... 438

INVESTIGATIONS ON THE SULPHON-PHTHALEÏNS:

II. *Dioxybenzoyl-benzene-sulphonic Acid and Sulphon-fluorescein.* By Charles C. Blackshear, ... 455

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE:

XXI. *The Carbohydrates of the Coffee Berry.* By Ervin E. Ewell, ... 473

NOTES.

Carl Schorlemmer (W. W. R.), ... 477

Iodosobenzoic Acid (W. W. R.), ... 478

The Preparation of Hydrazoic Acid (W. W. R.), ... 479

Jahrbuch der Chemie, ... 480

No. 7.

ON THE CONSTITUTION OF SODIUM ACET-ACETIC ETHER. By Arthur Michael, . . . 481

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON AROMATIC SILICIC ETHERS. By H. N. Stokes, . . . 545

NOTE ON BENZYL SILICATE. By H. N. Stokes, . . . 547

RESEARCHES ON THE SUGAR OF THE *Agave Americana*. By Gustave Michaud and José Fidel Tristan, . . . 548

REVIEWS.

SCIENTIFIC CORRESPONDENCE OF JOSEPH PRIESTLEY, . . . 551

A MANUAL OF CHEMISTRY, INORGANIC AND ORGANIC, WITH AN INTRODUCTION TO THE STUDY OF CHEMISTRY, . . . 551

THE PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS, . . . 552

No. 8.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, WORCESTER, MASS.:

- *The Addition-Products of Benzo- and of Toluquinone.* By T. H. Clark, . . . 553
- *The Condensation-Products of Acetacetic-Ether Hydrazide and of Oxalacetic-ether Hydrazide.* By Charles Walker, . . . 576

THE DECOMPOSITION OF SILVER CHLORACETATE CONSIDERED IN THE LIGHT OF OSTWALD'S THEORY OF AFFINITY. By J. H. Kastle, . . . 586

ON THE PREPARATION AND CONSTITUTION OF PARA-ANTHRACENE. By C. E. Linebarger, . . . 597

ON THE APPLICATION OF THE FRIEDEL-CRAFTS REACTION TO SYNTHESIS IN THE ANTHRACENE SERIES. By C. E. Linebarger, 602

THE DISSOCIATION OF SALTS INTO THEIR IONS BY WATER OF CRYSTALLISATION. By C. E. Linebarger, . . . 604

THE IODOMERCURATES OF ORGANIC BASES. By Albert B. Prescott, 606

TRIMETHYLXANTHINE AND SOME OF ITS DERIVATIVES. By Moses Gomberg, . . . 611

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA. No. XVIII. Communicated by F. P. Dunnington:

- 151.—*Analysis of Cuproplumbite from Butte City, Montana.* By J. T. De Bell, . . . 620
- 152.—*Analysis of Electric Calamine from Wythe County, Virginia.* By Archibald Jones, . . . 621
- 153.—*Analysis of Tschernozem or Black Soil.* By F. P. Dunnington and T. C. Whitlock, . . . 621
- 154.—*Analysis of Washing Powders.* By W. J. Kinney, W. H. Wenger and F. P. D., . . . 623

155.—*Solubility of Cream of Tartar in Diluted Alcohol.* By W. Wenger, ... 624
156.—*Analyses of Kale and Turnip Salad and Okra.* By J. D. Tinsley, ... 625
157.—*Analysis of Statuary Marble from Rutland, Vermont.* By Jno. T. De Bell, ... 626
158.—*Analyses of Glauconite from Hanover County, Virginia.* By M. B. Corse and Chas. Baskerville, . . . 627
159.—*Analysis of Paranthite from Clay County, North Carolina.* By W. N. Berkeley, ... 628
PROTEIDS OF THE FLAX-SEED. By Thomas B. Osborne, . . 629
CRYSTALLISED VEGETABLE PROTEIDS. By Thomas B. Osborne, . 662

INDEX TO VOLUME XIV, ... 691

VOL. XIV. [JANUARY, 1892.] No. 1.

AMERICAN CHEMICAL JOURNAL.

ON THE ISOMORPHISM AND COMPOSITION OF THORIUM AND URANOUS SULPHATES.

BY W. F. HILLEBRAND AND W. H. MELVILLE.

I.—CHEMICAL DISCUSSION.

BY W. F. HILLEBRAND.

During the course of an extended investigation on uraninite[1] it was often necessary to decompose the mineral in sealed tubes with sulphuric acid. At first a deposit was generally observed on removing the tubes from the oven, the character of which depended on the concentration of the acid and the presence or absence of thoria in the mineral. In the absence of this earth it took the form of a greenish powder with a strong acid, and of bright green, brilliantly reflecting crystals when a weak acid was used, unless the ratio of liquid to mineral was sufficiently high in the latter case to prevent crystallisation. As might naturally be supposed, these crystals were hydrated uranous sulphate. The best results as regards size of crystals were obtained with an acid containing one part of sulphuric acid to five or six of water by volume. With about 100 parts by weight of such an acid to one of the oxide UO_2, it might pretty confidently be expected that no crystallisation would take place.

In presence of thoria the green crystals still appeared, but they then contained thorium as well as uranium, and accompanying them was a beautiful, white, coherent, spongy mass, extending the length of the tube and consisting of a network of microscopic needles grouped in radiating bunches. This was likewise a double sulphate of uranium and thorium, resembling in every respect the deposit formed under similar conditions from a solution of thorium sulphate alone, except that when washed, dried, and compacted together there was a faint greenish tinge to it. Ordinarily the two forms of double salt appeared together, and it even seemed as if under favorable conditions, which have not yet been precisely determined, the crop of green crystals might be increased at the expense of the white deposit. At least on one occasion, when the heating was prolonged for several days, the latter gradually disappeared while the former increased in size and number. The white deposit always preceded the green crystals, and by regulation of the proportions of oxide and of acid, and of duration of heating, it is possible in practice to obtain the former alone, if desired.

---

[1] Bull. U. S. Geol. Survey, 78, 43, 1889-1890.

In order to secure material for exact chemical and crystallographical determinations, recourse was had to the artificially prepared oxides U_3O_8 and ThO_2, by using which, either alone or mixed in varying proportions, different products were obtained. Neither uraninite nor uranium dioxide, UO_2, is well adapted for this purpose, because of contamination of the crystals by sulphate of lead in the one case and by undissolved dioxide in the other. Even when using the oxide U_3O_8, care must be taken to avoid a like result, by fine pulverisation and avoidance of excess of oxide as compared with acid. So slightly soluble are the green crystals that over 50 per cent. of the dioxide UO_2 in uraninite, or in the oxide U_3O_8, can generally be obtained as sulphate. Hence it follows that when the dioxide is to be estimated volumetrically, care must be taken to use sufficient dilute acid to render impossible the formation of these crystals. The white, spongy deposit is not a hindrance to the exact estimation of the dioxide by potassium permanganate, for it dissolves readily in cold water, though with extreme slowness when once it has been compressed.

The green crystals were separated from their mother-liquor in a Gooch crucible, without asbestus felt, with the aid of suction; they were at once washed with hot dilute sulphuric acid, then with alcohol, and finally with ether. They were allowed to dry thoroughly in the air and were analysed in that condition. It was found by experiment that alcohol was practically without solvent action on the sulphates, and that none of the water of crystallisation was removed by it. If both forms of deposition occurred at one time, the spongy one was first removed with great ease by two or three rapid washings with cold water—the network of fine needles being partly dissolved and partly carried through the holes in the crucible by the powerful suction—after which alcohol and ether were used as before. The results of analyses were as follows:

	I.	Molecular ratio.	II.	Molecular ratio.
UO_2	49.18	1.00	48.40	1.00
ThO_2	3.59	...	5.58	...
SO_3	32.08	2.05	31.27	1.96
H_2O	14.18	4.04	14.84	4.13
	99.03		100.09	

A sample of uraninite decomposed by dilute sulphuric acid in a tube at about 170° C. furnished the product whose analysis is given under I. An earlier and very similar analysis of another preparation may be found on p. 50 of the bulletin cited. The loss is mainly, if not altogether, undetermined lead oxide from included lead sulphate, which accounts in part for the excess of SO_3 found. For No. II the oxides U_3O_8, ThO_2 were taken in such proportion that there should be about six times as much uranium dioxide as of thorium dioxide. Inasmuch as only 0.1622 gram was available for sulphuric-acid and water determinations in this analysis the ratio is not bad. One or two attempts to obtain a product with more thorium and less uranium by starting with correspondingly different proportions of the oxides ThO_2 and U_3O_8, were unsuccessful, perhaps because of the tendency of thorium sulphate to separate at once in the spongy state and thus to reduce the amount available for slow crystallisation with the uranium. The specific gravity of No. II was kindly determined by Mr. L. G. Eakins in alcohol of 0.7956 density. It was found to be 4.563 at 24.3° C., which, calculated for water at the same temperature as standard, becomes 3.63. The material examined contained 1.04 per cent. of the oxide U_3O_8 undissolved, which does not appear in the analysis, and, allowing for this a density of 7.3 (Clarke's Tables), that of the double sulphate having the given composition is found to be 3.61 at 24.3° C.

The uranium sulphate, of which the analysis is here given, was obtained by decomposing the oxide U_3O_8 with dilute sulphuric acid in the manner already mentioned. Its density was not ascertained.

	III.	Molecular ratio.
UO_2	53.99	1.00
SO_3	31.94	2.00
H_2O	14.13	3.94
	100.06	

It appears, as was to be expected, that thorium is capable of replacing uranium in the sulphate of the latter which holds in combination four molecules of water. That this is a true case of isomorphism is most fully shown by Mr. W. H. Melville in the crystallographical part of this paper, although the habit of the uranium sulphate differs from that of the double salt.

While, as above stated, failure resulted from attempts to lower the ratio between thorium dioxide and uranium dioxide in the green double salt, it was found that the spongy mass, which almost always formed in the tubes when thoriferous uraninite was decomposed with dilute sulphuric acid, contained a very much higher proportion of thorium, and that by taking the dioxides in varying proportions, double salts of correspondingly different composition could readily be obtained, as is shown by the following analyses:

	I.	Molecular ratio.	II.	Molecular ratio.
UO_2	34.34	1.00	16.92	1.00
ThO_2	19.84		36.07	
SO_3	31.48	1.95	32.66	2.05
H_2O(diff.)	14.34	3.95	14.35	4.01
	100.00		100.00	

Both salts were obtained from a mixture of the oxides U_3O_8 and ThO_2. In the case of No. II, the proportion was such that the uranium dioxide of the compound U_3O_8 was to the oxide ThO_2 as 2 to 1. It happened that the tube containing this preparation lay unopened for several weeks after removal from the oven, but during this time there had been no perceptible resolution of the precipitate, which on agitation made a thick emulsion with the acid. Both products were thrown on a Gooch crucible without asbestus felt, quickly washed twice or thrice with hot dilute sulphuric acid, and then with alcohol and ether, whereupon they were allowed to dry thoroughly in the air.

There is no reason to doubt the isomorphism of this salt with that formed under similar conditions from thorium alone, but whether these are crystallographically referable to the green crystals before described, or form a new case of dimorphism, must remain undetermined until the crystallographic features of the former are known. In polarised light, the needles of the double salt extinguish apparently parallel to their length.

Such contradictory statements appear in the literature of the subject regarding the composition of thorium sulphate separated from hot acid solutions—some authorities claiming 4½ molecules of water of crystallisation and others only 4—that it is very satisfactory to have evidence like that furnished by the above analyses to throw light upon the question. The tendency of late years has been to admit a mutual replaceability of thorium dioxide and uranium dioxide in chemical compounds, though no direct proof seems to have been heretofore established, and it was therefore reasonable to suppose that the composition of the thorium sulphate in question should correspond with that of the well-known uranous sulphate with 4 molecules of water. In the light of the above analyses there is no room to doubt the complete isomorphism of the two sulphates, and that Demarcay[1] and Roozeboom[2] were right in accepting the formula $ThO_4(SO_2)_2.4H_2O$, derivable from the more or less incomplete analyses of Berzelius, Berlin, and Chydenius, in preference to $ThO_4(SO_2)_2.4\frac{1}{2}H_2O$, afforded by the more numerous ones of Delafontaine.[3]

In possible explanation of Delafontaine's high results for water, Roozeboom[4] very justly remarks that because of its physical character the salt retains much mother-liquor, and that if this be not removed at a temperature above 45° C., the $9H_2O$ salt is formed from it on cooling, so that it is almost impossible not to find too much water. Notwithstanding numerous attempts to prepare the salt $ThO_4(SO_2)_2.4H_2O$ from hot acid solutions as well as from warm neutral ones, I have never myself succeeded in reducing the water to four molecules, even though the mass of needles was rapidly washed with hot dilute sulphuric acid and then with alcohol and ether, after freeing from mother-liquor by powerful suction on a Gooch crucible without asbestus felt, but my faith in the correctness of the formula with $4H_2O$ is not hereby shaken. A further possible cause of high results will appear from the following: The air-dried salt is said by Delafontaine to be thoroughly non-hygroscopic, and for a given temperature and hygrometric condition of the atmosphere it is true that no change in weight does occur; but if the salt be weighed from day to day, or even twice a day, a very marked gain or loss of weight is observed, depending in degree on the amount of change in the atmospheric conditions. In August and September, when hygrometric and thermometric readings were often high, and marked and rapid changes were not infrequent, this gain or loss sometimes amounted within 24 hours to over 0.5 per cent. of the total weight of the salt, and the extreme change during those months reached 1.22 per cent. It is therefore patent that the formula afforded by analysis may materially depend on whether the salt analysed was weighed when the weather was hot and moist or cold and dry.

---

[1] Compt. rend. **96**, 1860.

[2] Ztschr. phys. Chem. **5**, 198.

[3] Ann. Chem. (Liebig) **131**, 100. The statement by Kraut, near the foot of page 687 of Gmelin-Kraut's Inorganic Chemistry, Vol. II, Part I, is manifestly unwarranted. He considers the evidence in favor of the $4H_2O$ salt as insufficient, and thinks the analyses affording this formula were made upon mixtures which might have resulted through absorption of water by the $3H_2O$ salt. It is strange that individuality should have been accorded by Chydenius and Cleve to this latter salt, which the former obtained by drying over sulphuric acid, after washing with hot water, the precipitate formed by boiling a weakly acid solution of the sulphate. Roozeboom is certainly correct in excluding this $3H_2O$ salt from the list of thorium sulphates.

[4] Loc. cit., p. 202.

It may not be out of place here to call attention to a possible cause of the frequent discrepancies noticed in the statements of different writers in regard to the amounts of water given off by different substances when placed over sulphuric acid in a desiccator. No one would deny that sulphuric acid of maximum concentration is superior as a drying agent to the same acid somewhat, if only slightly, diluted; but it is probably not known to every one how much may depend on the strength of the acid used. A case in point is the following: A thorium sulphate containing, air-dried, 15.22 per cent. H_2O, or 4.23 molecules, lost weight over concentrated sulphuric acid in a tightly closed desiccator as shown in column I, and as in column II over acid which had been in use in another desiccator for a considerable length of time and was subsequently found to have a density of 1.66. The cases are not rigidly comparable perhaps because of the different times devoted to the experiments, which were not carried on simultaneously, but they serve to illustrate the point.

Time in days.	I. Acid of 1.84 sp. g.
1	3.80 per cent.
3	2.78
5	1.37
9	0.22
18	8.17

Time in days.	II. Acid of 1.66 sp. g.
1	2.87 per cent.
1	.40
3	.06
5	3.33

This may be considered an extreme case, but it shows plainly the importance of using fresh acid of full strength whenever experiments of this kind are to be made, in order that results may be properly comparable.

Similarly it is improbable that a highly hydrated substance, which loses much of its water at 100° C., would show as great a loss when dried in an ordinary air-bath as in a current of dry air of that temperature.

Another point to be considered when it is desired to find the maximum amount of water that can be removed by any drying agent in a desiccator (which of course as a method is in general inferior to that in which a continuous current of dry air or other gas is passed over the substance) is that, if many days are required for its removal—in other words, if the substance is slow to part with its moisture—the later weighings should not be made from day to day but at ever increasing intervals, otherwise a prematurely constant weight or even an increase may be observed. This is due to the fact that whenever the desiccator is opened, which must be twice for each weighing, it, at least in the upper part, becomes filled with moist air, and the substance itself may absorb some moisture before it can be returned to the desiccator; one or more days may then be required to restore the condition of equilibrium which obtained between the vapor tensions of water in the salt and in the air of the desiccator prior to opening the latter. Especially if the acid has become somewhat weakened is it possible for an increase to take place.

Originality is not claimed for the above observations on methods of drying, but it seems as if attention could not be too strongly or too frequently drawn to the points mentioned, which there is reason to fear are not always observed.

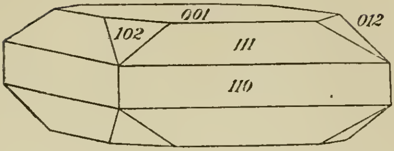
II.—Crystallographical Discussion.

By W. H. Melville.

The green crystals of sulphate of uranium and of the double sulphate of uranium and thorium described by Mr. Hillebrand are isomorphous and their crystallographic elements are almost identical. The angles between corresponding faces of the two salts differ by less than 1°, while their axial ratios are the same up to the second decimal place. Indeed, the axes plotted for the drawing of the crystals of one salt served for the drawing of those of the other.

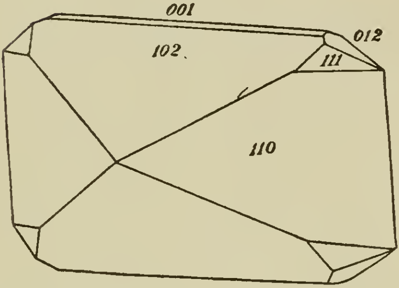
URANIUM SULPHATE.

1.



URANIUM-THORIUM SULPHATE.

2.



The two sulphates crystallise in the prismatic (orthorhombic) system. The habits of the two sets of crystals are quite unlike, and by simple inspection no analogy would seem to exist between them, since those of the double sulphate of uranium and thorium have all the appearance of the pyramidal (tetragonal) combination of forms.

On the goniometer the simple sulphate of uranium presented the most perfect faces, so that very accurate measurements were obtained. On the other hand the similar angles of the double sulphate showed great variations in the readings, often amounting to a difference of 40′ from the mean value. The difficulty of preserving in artificial crystals the same brilliancy of faces, after drying, which they possess in the mother-liquor, accounts for the broad bands of these reflect signals. However, after its system of crystallisation was identified, the mean of the most perfect and reliable measurements was taken.

The crystals of the double sulphate of uranium and thorium were often twinned, the twinning plane being parallel to (100). Also individuals occurred on the faces (102) and ($10\bar{2}$) which were composed of the face (110) in combination with minute planes of the forms (111) and (012).

The forms observed on the crystals of both salts were the same, but unequally developed, as the accompanying figures illustrate, in which the degree of development in the originals has been preserved. Forms: {001}, {010}—always a very narrow plane which does not appear in the drawings—{110}, {111}, {102}, {012}. Measurements:

(1) Uranium Sulphate.	Measured.	Calculated.
001 ∧ 111	70° 57′	70° 56′ 30″
001 ∧ 102	52° 13′	52° 10′ 7″
001 ∧ 012	33° 49′	33° 28′ 14″
111 ∧ 1$\bar{1}$1	51° 9′	fundamental.
111 ∧ 110	19° 3′ 30″	
110 ∧ 1$\bar{1}$0	54° 23′	54° 21′
102 ∧ 10$\bar{2}$	75° 34′	75° 39′ 46″

Axial ratio: $\breve{a} : \bar{b} : c = 1 : 1.9478 : 2.5755$.

(2) Double Sulphate of Uranium and Thorium.	Measured.	Calculated.
001 ∧ 102	51° 57′	51° 57′ 37″
001 ∧ 012	33° 25′	33° 39′ 38″
111 ∧ 1$\bar{1}$1	51° 46′	fundamental.
111 ∧ 110	19° 8′	
110 ∧ 1$\bar{1}$0	55° 14′	55° 2′ 24″
102 ∧ 10$\bar{2}$	76° 6′	76° 4′ 46″

Axial ratio: $\breve{a} : b : c = 1 : 1.9194 : 2.5563$.

LABORATORY OF THE U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C., *Nov.* 1891.

Contributions from the Chemical Laboratory of Purdue University.

VI.—THE DIGESTIBILITY OF THE PENTOSE CARBOHYDRATES.

BY W. E. STONE.

In some previous papers, attention has been called to the occurrence and properties of a class of bodies for which the names *pentosans* or *pentose carbohydrates* have been proposed.[1] It has been shown that they occur more or less abundantly in most plant tissues, and hence in many food materials; that they are soluble in dilute alkalies; that they are converted into sugar-like bodies by the action of dilute acids, and that these sugars (the pentoses) respond to many of the reactions for the true sugars or glucoses. In short, by the ordinary analytical operations they may easily elude recognition when accompanying the true carbohydrates. From this it is clear that a food-analysis, in which the "crude fibre," "crude protein," and "nitrogen free extract" have been determined by the ordinary methods, does not distinguish between these pentosans and such true carbohydrates as starch, sugar, etc. It is indeed possible, by the standard methods, to obtain apparently a large percentage of starch from materials which contain no starch whatever, the result being due to the presence of pentosans and the pentoses derived from them. But while these bodies are thus indiscriminately classified with others of quite different nature, so far as analytical results go, we are not justified in assuming that they possess equal nutritive value or digestibility. Indeed, in a general way, a low nutritive value has been ascribed to them, although there were few experimental facts to support such an assumption. Some twenty years ago, Gudkow recognised the presence of a body in wheat bran, which upon inversion yielded a sugar which was not glucose. In order to isolate it from the starch of the bran, he caused the latter to be fed to swine, and found that the unknown body actually resisted the digestive action to which the true carbohydrate succumbed.[1] He was unable to identify the body, but it has since been shown to be a pentosan from which arabinose may be derived.[2]

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[1] This Journal **12**, 435; **13**, 73 and 348. Ber. d. chem. Ges. **21**, 1572 and 2148; **23**, 2574 and 2791; **24**, 1657 and 3019. Ann. Chem. (Liebig) **249**, 227 and 257, J. Anal. and Appl. Chem. **5**, 421. Agric. Sci. **2**, 315; **5**, 91.

While recognising the existence of such bodies in vegetable food materials, it has hitherto been impossible to study their digestibility or physiological role experimentally, because of the lack of any analytical process by which they could be estimated separately from the other carbohydrates. Hence digestion experiments have exhibited this fallacy, viz., that while a homogeneity of composition and a constant value were assumed for the "nitrogen-free extract," it has been well known that it included a number of bodies of quite variable nature. This also holds true of the class of nitrogenous bodies classified as "crude protein," which are known to have a widely varying character and value, so far unrecognised in analytical methods save in a general division into albuminoids and non-albuminoids.[1]

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[1] Ztschr. Chem. [2] **6**, 360.

[2] Ann. Chem. (Liebig) **249**, 239; also Ber. d. chem. Ges. **23**, 3110.

Within a few years, however, specific qualitative reactions for the pentosans have been discovered, and one of these has of late been developed into a quantitative method of reasonable accuracy.[2] By this method it is possible to estimate the pentosans quite independently of the presence of accompanying carbohydrates, by converting them into furfurol, and titrating the latter with a solution of phenyl-hydrazine of known value. This, for the first time, renders possible the estimation of these bodies under all conditions, and allows analytical control of experiments as to their digestibility. Such an experiment has for the first time been carried out in this laboratory, and although simple in its details, the results seem worthy of record.

Rabbits were supplied with natural food containing appreciable quantities of pentosans, the amount and composition of both the food consumed and dung excreted being controlled by analysis. All of the ordinary rules controlling such experimentation were carefully observed. The experiment covered two periods, separated by a proper interval. The food selected for the first period consisted of a mixture of equal weights of wheat bran and cornmeal, the whole making a fairly normal sustenance ration. During the second period the food consisted of wheat bran alone. In both periods the bran supplied the desired pentosans, of which it contained sufficient quantities to produce 7.16 per cent. of furfurol. The two rabbits employed were fed with the specified food during six or eight days previous to the beginning of the periods in which the data were collected. During the feeding periods, all the food consumed was carefully weighed, and all the dung collected. The latter was afterwards weighed in an air-dry condition, corresponding to the state of the food. Finally, all of the materials were subjected to the ordinary fodder analysis, in addition to which the pentosans in all were determined by the method already cited.

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[1] Prof. Tollens has lately published in Die landwirthschaftlichen Versuchs-Stationen **39**, 401, an interesting resumé of the researches of himself and pupils, showing the varied character of these constituents of the "nitrogen-free extract," with their characteristic reactions. In closing he says: "In any case the old-style determination of the 'nitrogen-free extract,' however convenient and useful it may have been, requires modification at the present time."

[2] J. Anal. and Appl. Chem. **5**, 421.

The first period lasted ten days, and the food employed was the mixture of bran and meal. "Hans" consumed 533.8 grams and voided 118 grams of dung. "Max" consumed 344.0 grams and voided 71.8 grams of dung.

Analyses of the materials gave the following results:

	Food. Per cent.	Dung of Hans. Per cent.	Dung of Max. Per cent.
Moisture,	11.71	10.93	10.42
Ash,	3.71	9.45	9.92
Fibre,	5.42	16.48	19.43
Protein,	12.69	18.63	17.00
Ether extract,	4.03	2.07	1.64
N-free extract,	62.44	42.44	41.59
Furfurol obtained,	4.64	8.62	8.30
Pentosans (= furfurol × 1.38),	6.40	11.90	11.45
Proportion of pentosans in N-free extract,	10.25	28.04	27.53

The furfurol obtained stands for a certain amount of pentosans in the materials, but in just what proportion is not known. The purely theoretical assumption that the pentosans represented by the formula $(C_5H_8O_4)_n$ become pentoses, $(C_5H_{10}O_5)_n$, by hydrolysis, and these in turn furfurol, $(C_5H_4O_2)_n$, would fix the proportion of furfurol to pentosan as 1 to 1.38. Actually the proportion is much greater, since, by the rather destructive process by which the pentosans are converted into furfurol, the theoretical amount is far from realised. For the present purposes of this paper, however, it is sufficient to regard the percentages of furfurol as representing the pentosans part for part, although in some respects this undoubtedly makes too low a showing.

Referring to the analyses, it appears that "Hans" consumed a total amount of pentosans equivalent to 24.768 grams of furfurol, of which 10.172 grams were voided, and 14.596 grams, or 58.93 per cent., were digested.

"Max" consumed the equivalent of 15.862 grams of furfurol, of which 5.955 were voided, and 9.907 grams, or 62.46 per cent., were digested.

An interesting result of these analyses is the showing that, while the pentosans made up 10.25 per cent. of the nitrogen-free extract of the food, this proportion was increased to 27.53 and 25.68 per cent. in the dung, and yet the ordinary digestion experiment takes no cognisance of this change in relative composition.

Following the first period was a preliminary feeding with bran alone during eight days, preparatory to the second period of six days. During this period "Hans" consumed 415 grams of bran and voided 172.3 grams of dung. Following are the analytical data:

	Bran.	Dung.
Moisture,	11.06 per cent.	14.22 per cent.
Ash,	7.40	9.50
Fibre,	9.91	19.27
Protein,	16.00	11.00
Ether extract,	4.36	2.34
N-free extract,	51.27	43.67
Furfurol obtained,	7.16	10.59
Pentosans (= furfurol × 1.38),	10.88	14.61
Proportion of pentosans in N-free extract,	21.22	33.46

In this period "Hans" consumed pentosans equivalent to 29.743 grams of furfurol, of which 18.247 grams were voided and 11.496 grams were digested. The proportion of pentosans in the nitrogen-free extract of the food (21.22 per cent.) was increased to 33.46 per cent. in the dung.

These results show that the pentosans are, to a marked degree, less digestible than the true carbohydrates, with which they have been indiscriminately classified. In the first period about 60 per cent. was digested, but in the second period, when the proportion of nitrogenous to carbonaceous matter was considerably increased, the pentosans did not seem able to supply the lack of carbohydrates and were themselves less than 40 per cent. digestible. Perhaps the most important result is that indicating the difference in composition between the "nitrogen-free extract" of the food and that of the dung. In digestion experiments these are assumed to be of the same character and the diminution in amount after passing the digestive tract is charged up roundly to the digestibility of the carbohydrates, whereas the digestive action has been selective and only certain constituents of the nitrogen-free extract have been removed, while others remain wholly or in part unchanged. No comparison of the analytical data is complete which fails to take into account the changed composition of the nitrogen-free extract.

These somewhat meagre data are submitted here for their suggestiveness in a field in which little has been done, and also as illustrating the desirability of some analytical method more specific than the one now in use for the control of food valuations and digestion experiments.

CARBON DIOXIDE IN THE URINE.

By T. C. Van Nüys and R. E. Lyons.

To what is the alkalinity of normal urine ordinarily due? The student who would seek a solution of this question in medical literature will find the subject evaded, or the statement made that the urine is alkaline from the presence of the carbonates of the metals of the alkalies.

Our attention was first directed to this subject in preparing chemically pure normal urates of potassium and sodium ($C_5H_2N_4K_2O_3$, $C_5H_2N_4Na_2O_3$). We found that these salts are intensely alkaline in reaction, and knowing that the uric acid in normal urine is occasionally combined with these metals as normal urates, we were led to believe that the alkalinity of normal urine is due in part to the presence of normal urates, and that carbon dioxide in combination is not necessarily a constituent of normal urine, otherwise from urine distinctly alkaline in reaction, acid urates would separate. In order that in our researches an error might not be committed, we studied the properties of the normal urates of potassium and sodium.

Properties of the normal urates.—When either salt is dissolved in distilled water, the solution is intensely alkaline, not differing in this respect from strong solutions of either the hydrates or the carbonates of potassium and sodium.

On passing a current of carbon dioxide through a concentrated solution of either salt a white precipitate forms, which is at first the acid urate, $C_5H_3N_4KO_3$ or $C_5H_3N_4NaO_3$.

A strong solution of either normal salt yields a precipitate of the acid urate when treated with calcium acid phosphate, $CaH_4(PO_4)_2$.

Properties of the acid urates of potassium and sodium.—On introducing carbon dioxide into a concentrated aqueous solution of potassium or sodium acid urate, uric acid slowly separates. A strong solution of sodium hydrogen carbonate brings about decomposition of the acid urates in the same manner. The acid urate of either metal in aqueous solution is decomposed by means of calcium acid phosphate with the liberation of uric acid. On dissolving 90 mg. of the acid urate of sodium in 100 cc. distilled water and adding 300 mg. calcium acid phosphate, uric acid begins to separate in 8 minutes. If, however, 3 grams of pure urea be dissolved in the water with the acid urate before the acid phosphate is introduced, the decomposition of the acid urate does not begin within 20 minutes. The temperature at which the reaction took place was 16°-19° C.

Deportment of the acid phosphates and carbonates.—When a solution of the acid phosphate of sodium or calcium is introduced into a solution of either the mono- or dicarbonate of potassium or sodium, carbon dioxide is liberated, and if sufficient acid phosphate be introduced the solution becomes acid in reaction. The acid sulphate of potassium or of sodium acts in the same manner. Although the acid urates of potassium and sodium contain each an atom of hydrogen which is displaceable by a metal, yet these salts are neutral or *very* slightly acid in reaction.

From the properties of the salts above enumerated we were led to believe that carbon dioxide in acid urine is always in the free state, and never in combination; and that as di- and basic potassium or sodium phosphates, as well as the normal urates of these metals, are intensely alkaline in reaction, the carbon dioxide is in all probability not in combination in moderately alkaline urine, but is combined in urine strongly alkaline.[1]

To determine this question, the carbon dioxide in the urine of one of us (L.) was estimated after employing (1) a mixed diet, (2) a vegetable diet, (3) after ingesting large doses of the neutral tartrate of sodium, $C_4H_4Na_2O_6$.

The following are the quantities of carbon dioxide estimated in the total urine of periods of 24 hours, for six consecutive days, with a mixed diet. The urine was acid in reaction during the whole time, 6 days:

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[1] Neubauer states in his "Analyse des Harns" (8th edition, p. 106-7) that in acid urine, a part of the bases are in the form of bi-carbonates—hence carbon dioxide in combination.

First day, ...	0.64	gram	CO_2.
Second day, ...	0.49	"	"
Third day, ...	0.60	"	"
Fourth day, ...	0.56	"	"
Fifth day, ...	0.45	"	"
Sixth day, ...	0.79	"	"

Average for each period, 0.588 gram CO_2.

With a diet distinctly vegetable, urine strongly alkaline in reaction, the carbon dioxide increased, but when the urine was rendered acid no effervescence of carbon dioxide occurred. The basic phosphates were precipitated. The following quantities of carbon dioxide were determined in the urine of each period of 24 hours:

First day, ...	1.20	grams	CO_2.
Second day, ...	1.16	"	"
Third day, ...	0.93	gram	"

Average for each period, 1.09 grams CO_2.

By ingesting 10 to 15 grams neutral sodium tartrate in 24 hours, the urine became strongly alkaline in reaction. During two periods of 48 hours each, two consecutive days, the neutral tartrate of sodium was taken in large doses.

The following are the quantities of the salt taken, and the number of grams of carbon dioxide in the urine of 24 hours:

First period 48 hours following "mixed diet."	Grams $C_4H_4Na_2O_6$ taken in 24 hours.	Grams CO_2 in urine of 24 hours.
1st day,	10	1.42
2d "	10	1.65
Second period 48 hours following vegetable diet.		
1st day,	15	1.30
2d "	15–17	2.67

From the results it is seen that in acid urine a relatively small quantity of carbon dioxide was found; that with a vegetable diet more carbon dioxide appeared in the urine; and that with large doses of sodium neutral tartrate the urine became alkaline, which was in part due to carbonates, as the urine effervesced slightly on the addition of an acid.

When the phosphoric, sulphuric and uric acids were present in the form of normal or basic salts, and as the blood was strongly alkaline by the presence of an unusual quantity of sodium bicarbonate, either sodium hydrate would necessarily appear in the urine, or carbon dioxide be combined with the excess of sodium, as was the case. It is a well recognised fact that the kidneys are the only emunctories through which notable quantities of the metals of the alkalies are eliminated.[1]

To transform the average quantities of phosphoric and uric acids in acid compounds in the urine of 24 hours into basic, or normal, salts without combined carbon dioxide, a relatively large quantity of sodium hydrate would be required, as is readily shown by the following table:

Quantity of acid salts in grams in the urine in 24 hours.	Acid Salts in the Urine in 24 Hours.
3.2634	$CaH_4(PO_4)_2 + 2CaCl_2 + \overset{(2.2506)}{4NaOH} = Ca_3(PO_4)_2 + 4NaCl + 4H_2O.$
1.1146	$NaH_2PO_4 + \overset{(0.7430)}{2NaOH} = Na_3PO_4 + 2H_2O.$
2.20408	$NaHSO_4 + \overset{(0.7346)}{NaOH} = Na_2SO_4 + H_2O.$
0.9046	$C_5H_3NaN_4O_3 + \overset{(0.1904)}{NaOH} = C_5H_2Na_2N_4O_3 + H_2O.$

The numbers in parenthesis over the NaOH are the quantities in grams of the alkali required to transform the acid salts into normal or basic salts. By adding these numbers it is found that to render alkaline the quantity of urine secreted in 24 hours, containing the average quantities of acids and bases, 3.9186 grams sodium hydrate are required.

In this connection it is seen that 2.9852 grams sodium hydrate of the total quantity (3.9186) are utilised in transforming the acid phosphate of calcium (including the equivalent of acid phosphate of magnesium) and the acid sulphate of sodium (including the equivalent of acid sulphate of potassium) without imparting alkalinity to the urine. The remainder, 0.9334 gram sodium hydrate, forms intensely alkaline salts. It is, however, doubtful if it ever occurs that all of the phosphoric, sulphuric and uric acids in the urine pass into acid compounds before ammonia makes its appearance in abnormal quantities.

From this table it is seen that in cases where the urine is strongly acid, and it is desired to render the urine alkaline by medication, small quantities of the tartrates, or acetates of sodium, or of potassium, will, in all probability, fail to accomplish the desired result. With the acid phosphates and sulphates the normal urates cannot long remain. When in distilled water, in quantities in which they usually are in acid urine, they decompose normal urates in a few minutes, but by the presence of urea and other bodies in urine the action is retarded. Owing to this, urine, at first strongly acid from the presence of the acid phosphates and sulphates, although when cooled to ordinary temperatures, often has no sediment; but after the lapse of a few hours a heavy sediment of acid urates forms, and as the acid urates are scarcely acid in reaction, the urine by this change becomes less acid in reaction. The acid urates remaining in solution are slowly acted upon by the acid salts yet remaining. Probably the retarded action is due to the dilution of the acid salts. The reaction of the acid salts with the carbonates is so much more energetic that the latter would certainly be decomposed in the urine while yet in the bladder.

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[1] Salkowsky: Centrbl. Med. Wiss., 1871, p. 289. Ref. Ztschr. anal. Chem. **10**, 378.

When the urine is alkaline from the presence of normal urates and basic, or "neutral," phosphates of the metals of the alkalies, carbon dioxide cannot exist firmly combined unless the metals of the alkalies are in quantities greater than sufficient to saturate the uric and phosphoric acids; otherwise uric acid, or acid urates of the metals of the alkalies, would separate as a sediment with the basic phosphates of calcium and magnesium. As the matter stands, however, there is no evidence that carbon dioxide may not be loosely combined with bases in alkaline urine, but not in a degree sufficient to cause the separation of the acid urates, or uric acid.

It is a well recognised fact in chemical science that when an equivalent of an acid is added to a normal salt in solution, the acid added, if it form a soluble salt with the base, does not set free the combined acid, although the acid added may be considered the stronger acid of the two. The base will be divided between the acids in certain proportions. Volatility of a product, however, is a modifying factor in the case. Owing to the fact that carbon dioxide exerts, in the presence of acid salts, dissociation-pressure, which is greater in degree than the attraction it has for bases, normal urates are not decomposed by it. However, in the absence of acid salts in the urine, according to the law which governs the relative affinity of acids for bases, there is no evidence based on experiment to disprove the hypothesis that carbon dioxide may be, in limited quantity, feebly combined with bases associated with phosphoric, sulphuric, and uric acids in alkaline urine, but not sufficiently combined to set free either acid urates or uric acid. If the latter were true, acid urates of potassium and sodium and free uric acid would often be a sediment in alkaline urine, which is never the case.

Admitting the hypothesis that carbon dioxide may be feebly combined in urine which is alkaline but does not contain bases in quantities exceeding the saturating capacity of the acids present, with the exception of carbon dioxide, then we can explain why in our researches we found that carbon dioxide was in increased quantities in urine slightly alkaline from a vegetable diet.

From our investigations we conclude:

1st. Combined carbon dioxide is not ordinarily a constituent of normal urine.

2d. When carbon dioxide does appear in the urine combined, it is owing to excessive alkalinity of the blood when it is induced to combine with the hydrates of potassium and sodium, which would otherwise appear in the urine. The case is analogous to that of the neutral or even acid condition of the blood when ammonia appears in abnormal quantity, combined with acids.[1]

3d. Alkalinity of normal urine, unless excessive in degree, is caused by di- or tri-basic potassium, or sodium phosphates, and by normal urates of potassium and sodium.

CHEMICAL LABORATORY OF THE INDIANA UNIVERSITY, *November*, 1891.

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[1] Frey: Centrbl. Med. Wiss., 1872, p. 833. Kurtz: Ueber Entziehung von Alkalien aus dem Thierkörper, Inaug. Diss., Dorpat, 1874. Walter: Archiv. f. exper. Pathologie u. Phar. **7**, 148. Gathgens: Ztschr. physiol. Chem. **4**, 36-54. E. Hallervorden: Arch. exper. Path. **12**, 237-275.

Contributions from the Sheffield Biological Laboratory of Yale University.

A STUDY OF THE PROTEIDS OF THE CORN OR MAIZE KERNEL.

By R. H. Chittenden, Ph. D., *Professor of Physiological Chemistry in Yale University*, and Thomas B. Osborne, Ph. D., *Chemist at the Connecticut Agricultural Experiment Station.*

(Continued from p. 552, Vol. 13.)

II.—Proteids Soluble both in Water and in Dilute Salt Solutions.

An aqueous extract of corn meal, as well as a sodium chloride extract, contains in addition to the globulins already described more or less proteid matter soluble in water alone and having the general properties of ordinary albumin and proteose. These bodies can be detected, either in the original extract after the complete removal of all globulin, or better in the ammonium-sulphate precipitate of the mixed proteids, after the globulins and their alteration-products have been entirely separated by dialysis and filtration.

Of albumin-like bodies there would appear to be two present, both more or less coagulable by heat, but unlike in chemical composition. Moreover, one is precipitable by the addition of dilute acetic or hydrochloric acid to a 10 per cent. sodium-chloride solution, after the globulins have been entirely removed, while the other remains in solution and can be advantageously separated only by coagulation of the neutralised fluid. From the albumin-free solution, the proteose can be separated by saturation with sodium chloride and addition of a little acetic, or hydrochloric acid.

An aqueous solution containing these water-soluble proteids is precipitated on saturation with ammonium sulphate, and on addition of alcohol, but not by saturation with sodium chloride. Addition of 0.2-per cent. hydrochloric acid or 30-per cent. acetic acid likewise gives no precipitate. Heated gradually, an aqueous solution of these proteids becomes turbid at about 46°, with separation of a flocculent precipitate at 60°. Between 60° and 70° a fairly large coagulum separates. The fluid again becomes turbid about 85°, and on boiling, a slight coagulum appears which gradually increases as the boiling is continued. In fact, it is very difficult to make a complete coagulation. The solution may be evaporated nearly to dryness, the residue taken up in water and filtered, and then on boiling this solution for some time an additional coagulum may appear. Indeed, there is every evidence of some kind of transformation in the process of coagulation, or possibly it may be that we have to deal simply with a body very slowly, or incompletely, coagulable by heat, like some forms of phyt-albumose.

Preparation A.—The proteids precipitated from a sodium-chloride extract of 5 kilos. of corn meal, by means of ammonium sulphate, were dissolved in water and 10-per cent. solution of sodium chloride, and dialysed until every trace of globulin and soluble salts had been removed. To the clear neutral fluid thus obtained, which gave no precipitate whatever on the addition of dilute acid or on saturation with sodium chloride, pure, crystallised salt was added in such quantity that the solution contained 10 per cent. of sodium chloride, after which the clear fluid was rendered slightly acid with 0.2-per cent. hydrochloric acid. The precipitate thus produced was filtered off, treated with water in which, or in the slightly acid fluid which resulted, it was mainly soluble, and the solution carefully neutralised with a few drops of very dilute sodium carbonate. This gave rise to an abundant precipitate which was filtered off, washed thoroughly with water, alcohol and ether, weighing, when air-dry, 2.48 grams (Albumin A^1). This substance, when first precipitated by neutralisation, was very readily soluble in dilute sodium carbonate, but after becoming dry it was wholly insoluble in the dilute alkaline fluid.

This description affords a very good illustration of the readiness with which some of these vegetable proteids undergo change by mere contact with dilute acids or alkalies. Evidently, the addition of a little 0.2-per cent. acid to the salt solution of these proteids gives rise to an acid compound of one of the albumins insoluble in salt solution (10-per cent.), but soluble in water or, rather, in the slightly acid fluid. Withdrawal of the acid, however, by neutralisation with a few drops of very dilute sodium carbonate, yields not the original albumin, but apparently an insoluble acid-albumin; a reaction more characteristic of a globulin than of a genuine albumin.

The 10-per cent. sodium-chloride solution, from which the above albumin was precipitated by the addition of 0.2-per cent.

hydrochloric acid, was heated to boiling, when there resulted a coagulum which, after being washed with hot water until free from salt, and then with alcohol and ether, weighed air-dry, 1.03 grams (Albumin A^2).

On boiling the filtrate from this latter coagulum, no further precipitate could be obtained, but saturation of the slightly acid fluid with salt gave a considerable precipitate, readily soluble in water. The substance thus precipitated was therefore dissolved in water and dialysed until the sodium chloride was entirely removed. The salt-free solution was then evaporated to dryness on a water-bath. As the solution became concentrated, a portion of the proteid separated as a scum or skin on the surface of the fluid, eventually making an insoluble coagulum. On treating the dried residue with water, still more insoluble matter appeared, showing that either all of the coagulable albumins (Albumins A^1 and A^2) had not been removed from the fluid, or else that in the process of treatment changes were going on by which new coagulable matter was being formed. Eventually, however, by evaporating the filtered fluid to dryness several times and taking up the residue in water, there resulted a solution of a proteid body which showed no signs of coagulation, even on long-continued heating, and which yielded a gummy precipitate on the addition of absolute alcohol. This proteose-like body was, however, obtained in very small quantity—only about 0.3 gram—and might be considered as possibly formed by the hydrolytic action of the repeated evaporations, etc.

On the other hand, it might perhaps be claimed with equal plausibility that the slow coagulations witnessed above were the result of a regressive metamorphism of a proteose normally present in the corn-kernel.

The two albumins, A^1 and A^2, were dried at 110° C. and analysed with the following results:

Analysis of Albumin A^1.

I. 0.3828 gram substance gave 0.2355 gram $H_2O = 6.84$ per cent. H, and 0.7398 gram $CO_2 = 52.71$ per cent. C.

II. 0.3454 gram substance gave 43.4 cc. N at 3.0° C. and 761.7 mm. pressure $= 15.64$ per cent. N.

III. 0.3185 gram substance gave 39.4 cc. N at 2° C. and 768.5 mm. pressure $= 15.60$ per cent. N.

IV. 0.3292 gram substance gave 0.0010 gram ash $= 0.30$ per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	52.86	..	..	52.86
H	6.86	..	..	6.86
N	..	15.69	15.65	15.67
S	..	..	..	24.61
O	..	..	..	
				100.00

Analysis of Albumin A^2.

I. 0.2355 gram substance gave 0.1430 gram $H_2O = 6.76$ per cent. H, and 0.4464 gram $CO_2 = 51.72$ per cent. C.

II. 0.3498 gram substance gave 45.9 cc. N at 3° C. and 758.5 mm. pressure = 16.27 per cent. N.

III. 0.3214 gram substance gave 0.0013 gram ash = 0.40 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	51.93	..	51.93
H	6.79	..	6.79
N	..	16.33	16.33
S	..	..	24.95
O	..	..	
			100.00

Preparation B.

Another series of similar products was made as follows: 6.5 kilos. of finely ground corn were extracted first with water and then with 10-per cent. salt solution. From these two extracts the proteids were precipitated by saturation with ammonium sulphate, the precipitates dissolved separately, so far as possible, in water and 10-per cent. salt solution, and the globulins separated by thorough dialysis. In the two filtrates, wholly free from globulin, the addition of an equal volume of 20-per cent. salt solution and a little 0.2-per cent. hydrochloric acid produced a flocculent precipitate, considerably heavier in the aqueous extract than in the sodium-chloride extract. As the two precipitates, however, were apparently the same, they were united and dissolved, so far as possible, in water. In this case, unlike the preceding experiment, a large proportion of the precipitate did not dissolve in the water added, apparently because the fluid was not sufficiently acid. This insoluble portion, after being washed with water, was therefore dissolved in a little 0.2-per cent. hydrochloric acid and the solution carefully neutralised with dilute sodium carbonate, by which the substance was reprecipitated. After being washed thoroughly with water, alcohol and ether, it weighed, air-dry, 2.67 grams (Albumin B^1).

On analysis, after drying at 110° C., it yielded the following results:

Analysis of Albumin B^1.

I. 0.3274 gram substance gave 0.1992 gram $H_2O = 6.75$ per cent. H, and 0.6369 gram $CO_2 = 53.05$ per cent. C.

II. 0.3133 gram substance gave 0.1900 gram $H_2O = 6.74$ per cent. H, and 0.6081 gram $CO_2 = 52.92$ per cent. C.

III. 0.4413 gram substance gave 54.8 cc. N at 20° C. and 762.1 mm. pressure $= 15.53$ per cent. N.

IV. 0.4758 gram substance gave 0.0048 gram ash $= 1.01$ per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	53.58	53.48	..	53.53
H	6.82	6.81	..	6.82
N	..	..	15.69	15.69
S	..	..	..	23.96
O	..	..	..	
				100.00

The two original acid filtrates, from which the above albumin was separated, were in this preparation directly saturated with sodium chloride, and the precipitate of the residual albumin and proteose filtered off and dissolved in water. The resultant solutions were united, neutralised and dialysed until the salts were entirely removed. At the end of the dialysis, a small amount of substance was found adhering to the walls of the dialyser, not, however, sufficient in quantity to do anything with. On evaporation of the filtered fluid to half its volume considerable coagulum formed, which was washed with water, alcohol and ether, weighing, when air-dry, 1.32 grams (Albumin B^2). On further evaporation of the mother-liquor containing the proteose an additional coagulum formed, which was added to the preceding.

This preparation, dried at 110° C., gave on analysis the following results:

Analysis of Albumin B^2.

I. 0.2387 gram substance gave 0.1453 gram $H_2O = 6.76$ per cent. H, and 0.4547 gram $CO_2 = 51.95$ per cent. C.

II. 0.3546 gram substance gave 47.6 cc. N at 3° C. and 751.8 mm. pressure = 16.49 per cent. N.

III. 0.3868 gram substance gave 0.0008 gram ash = 0.21 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	52.06	..	..	52.06
H	6.77	..	..	6.77
N	..	16.53	..	16.53
S	..	..	..	24.64
O	..	..	..	
				100.00

In the filtrate from which this last body was obtained there still remained some coagulable matter, which was finally completely removed by careful heating on a water-bath. The concentrated and perfectly neutral fluid was then precipitated with absolute alcohol, and the resultant proteose collected and washed with alcohol and ether.

This substance, like the soluble proteoses formed from animal proteids, was especially characterised by extreme solubility in water, non-coagulability by heat, etc. It was precipitated by acetic acid and potassium ferrocyanide, by alcohol, phosphotungstic acid, etc., and gave the usual proteid reactions with Millon's reagent, and with cupric sulphate and potassium hydroxide.

Dried at 110° C. until of constant weight, the product, separated as just described, gave on analysis the following results:

Analysis of Proteose B.

I. 0.3390 gram substance gave 0.1952 gram H_2O = 6.40 per cent. H, and 0.6154 gram CO_2 = 49.51 per cent. C.

II. 0.3409 gram substance gave 0.1993 gram H_2O = 6.49 per cent. H, and 0.6158 gram CO_2 = 49.27 per cent. C.

III. 0.3326 gram substance gave 41.3 cc. N. at 2.5° C. and 760.9 mm. pressure = 15.49 per cent. N.

IV. 0.2984 gram substance gave 37.4 cc. N at 4° C. and 758.5 mm. pressure = 15.49 per cent. N.

V. 0.2784 gram substance, fused with $KOH + KNO_3$, gave 0.0520 gram $BaSO_4$ = 2.57 per cent. S; deducting 0.25 for S in the ash = 2.32 per cent. S.

VI. 0.4206 gram substance gave 0.0120 gram ash = 2.42 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	50.74	50.50	..	..	..	50.62
H	6.56	6.65	..	..	..	6.61
N	..	..	15.88	15.88	..	15.88
S	..	..	..	..	2.37	2.37
O	..	..	..	..	..	24.52
						100.00

Preparation C.

These same bodies were prepared again, on a somewhat larger scale, from 25 kilos. of finely ground corn. The process was as follows: The meal was extracted directly with an abundance of 10-per cent. salt solution, and the proteids precipitated collectively by saturation of the fluid with ammonium sulphate. The precipitate was dissolved in water and salt solution, and the fluid dialysed about three weeks, until the salts were entirely removed and the globulins completely separated.

The salt-free solution, containing the albumins and proteose, was then treated with sodium chloride until the mixture contained 10 per cent. of salt, after which 0.2-per cent. hydrochloric acid was added until the precipitation was complete. The albumin so separated was filtered off and treated with water, in which about four-fifths of it dissolved. The residue, however, was dissolved in a little 0.2-per cent. hydrochloric acid and the two solutions united, and dialysed until free from chlorides. At the end of the dialysis the fluid was perfectly neutral, and the albumin (obviously altered), or a portion of it, was found precipitated in the parchment tube, the same as on neutralisation of the slightly acid fluid described in the previous preparations, while in the solution was found considerable non-coagulable proteose which must have been carried down with the albumin. The precipitate (Albumin C^1) was filtered off, washed thoroughly with water, alcohol and ether, and dried at 110° C. for analysis. Air-dry, it weighed 3.14 grams.

Analysis of Albumin C^1.

I. 0.3459 gram substance gave 0.2102 gram $H_2O = 6.75$ per cent. H, and 0.6714 gram $CO_2 = 52.93$ per cent. C.

II. 0.3649 gram substance gave 0.2222 gram $H_2O = 6.77$ per cent. H, and 0.7065 gram $CO_2 = 52.81$ per cent. C.

III. 0.3546 gram substance gave 43 cc. N at 774.0 mm. pressure = 15.35 per cent. N.

IV. 0.6957 gram substance fused with KOH + KNO_3 gave 0.0750 gram $BaSO_4 = 1.48$ per cent. S.

V. 0.4331 gram substance gave 0.0016 gram ash = 0.37 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	53.12	53.00	..	..	53.06
H	6.78	6.80	..	..	6.79
N	..	..	15.41	..	15.41
S	..	..	..	1.48	1.48
O	..	..	..	..	23.26
					100.00

The proteose precipitated with the above albumin was separated from the concentrated solution, after removal of all coagulable matter, by precipitation with absolute alcohol. It weighed, air-dry, 2.5 grams and gave on analysis, after drying at 110° C., the following results:

Analysis of Proteose C^1.

I. 0.3131 gram substance gave 0.1903 gram $H_2O = 6.75$ per cent. H, and 0.5717 gram $CO_2 = 49.80$ per cent. C.

II. 0.3783 gram substance gave 0.2276 gram $H_2O = 6.69$ per cent. H, and 0.6873 gram $CO_2 = 49.55$ per cent. C.

III. 0.3397 gram substance gave 43.5 cc. N at 3° C. and 770.7 mm. pressure = 16.13 per cent. N.

IV. 0.7246 gram substance fused with KOH + KNO_3 gave 0.0837 gram $BaSO_4 = 1.58$ per cent. S.

V. 0.4632 gram substance gave 0.0131 gram ash = 2.83 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	51.25	51.00	..	..	51.13
H	6.94	6.88	..	..	6.91
N	..	..	16.59	..	16.59
S	..	..	..	1.62	1.62
O	..	..	..	..	23.75
					100.00

The original filtrate from the precipitate produced by dilute hydrochloric acid in the presence of 10-per cent. sodium chloride was dialysed until nearly free from salt, and then, being perfectly neutral to test-papers, was concentrated to one-third its volume and filtered from the coagulum which resulted. This coagulum

(Albumin C^2) was washed thoroughly with water, alcohol and ether, and after being dried at 110° C. was analysed. Air-dry it weighed 2.28 grams.

Analysis of Albumin C^2, First Coagulum.

I. 0.3226 gram substance gave 0.1927 gram $H_2O = 6.64$ per cent. H, and 0.6092 gram $CO_2 = 51.50$ per cent. C.

II. 0.3293 gram substance gave 0.1985 gram $H_2O = 6.69$ per cent. H, and 0.6195 gram $CO_2 = 51.31$ per cent. C.

III. 0.3737 gram substance gave 46.3 cc. N at 3° C. and 774.2 mm. pressure = 15.68 per cent. N.

IV. 0.4015 gram substance gave 0.0038 gram ash = 0.94 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.97	51.78	..	51.88
H	6.70	6.75	..	6.73
N	..	..	15.89	15.89
S	..	..	..	25.50
O	..	..	..	
				100.00

The filtrate from the above coagulum was concentrated still further, without giving any appreciable coagulum, then saturated with salt and precipitated by the addition of 0.2-per cent. hydrochloric acid. The precipitate was dissolved in water, dialysed until the salt had been entirely removed, and then evaporated to dryness on the water-bath. During this last evaporation a considerable coagulum formed, which was collected, washed, dried and analysed. It weighed 1.22 grams (Albumin C^2, second coagulum).

Analysis of Albumin C^2, Second Coagulum.

I. 0.4488 gram substance gave 0.2600 gram $H_2O = 6.44$ per cent. H, and 0.8224 gram $CO_2 = 49.98$ per cent. C.

II. 0.3050 gram substance gave 41.8 cc. N at 3° C. and 755.8 mm. pressure = 16.93 per cent. N.

III. 0.3769 gram substance gave 0.0077 gram ash = 2.04 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.02	..	..	51.02
H	6.57	..	..	6.57
N	..	17.28	..	17.28
S	..	..	..	25.13
O	..	..	..	
				100.00

From the concentrated filtrate from this second coagulum, a small amount of proteose was separated by addition of absolute alcohol. Dried at 110° and analysed, it gave the following results:

Analysis of Proteose C^2.

I. 0.3666 gram substance gave 0.2065 gram $H_2O = 6.26$ per cent. H, and 0.6435 gram $CO_2 = 47.87$ per cent. C.

II. 0.3333 gram substance gave 0.1901 gram $H_2O = 6.34$ per cent. H, and 0.5934 gram $CO_2 = 48.55$ per cent. C.

III. 0.3654 gram substance gave 46.3 cc. N at 3° C. and 768.9 mm. pressure = 15.93 per cent. N.

IV. 0.4266 gram substance gave 0.0159 gram ash = 3.72 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	49.72	50.42	..	50.07
H	6.50	6.58	..	6.54
N	..	..	16.54	16.54
S	..	..	..	26.85
O	..	..	..	
				100.00

Preparation D.

Another experiment after the same order as the preceding was carried out without, however, yielding sufficient of any one product for analysis, except of the albumin coagulable by heat present in the filtrate from the precipitate produced by 10-per cent. salt solution and dilute acid.

This product (Albumin D^2) was analysed for the sake of additional confirmatory evidence, with the following results

Analysis of Albumin D^2, Coagulum.

I. 0.4274 gram substance gave 0.2584 gram $H_2O = 6.71$ per cent. H, and 0.8055 gram $CO_2 = 51.39$ per cent. C.

II. 0.3735 gram substance gave 0.2278 gram $H_2O = 6.77$ per cent. H, and 0.7076 gram $CO_2 = 51.66$ per cent. C.

III. 0.3739 gram substance gave 49.8 cc. N at 17.3° C. and 757 mm. pressure = 15.67 per cent. N.

IV. 0.3783 gram substance gave 51.1 cc. N at 18.2° C. and 755.1 mm. pressure = 15.80 per cent N.

V. 0.3450 gram substance gave 0.0013 gram ash = 0.38 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	51.58	51.84	..	..	51.71
H	6.73	6.79	..	..	6.76
N	..	..	15.72	15.85	15.78
S O	..	..	..	..	25.75
					100.00

The relationship in composition of these several products can be seen from the following table:

Albumin Precipitated by Salt and Acid.

	A^1.	B^1.	C^1.
C	52.86	53.53	53.06
H	6.86	6.82	6.79
N	15.67	15.69	15.41
S O	24.61	23.96	1.48 23.26

Albumin Coagulated by Heat.

	A^2.	B^2.	C^2, 1st.	C^2, 2d.	D^2.
C	51.93	52.06	51.88	51.02	51.71
H	6.79	6.77	6.73	6.57	6.76
N	16.33	16.53	15.89	17.28	15.78
S O	24.95	24.64	25.50	25.13	25.75

Proteose.

	B.	C^1.	C^2.
C	50.62	51.13	50.07
H	6.61	6.91	6.54
N	15.88	16.59	16.54
S O	2.37 24.52	1.62 23.75	26.85

We are so firmly convinced that these bodies are, in part at least, the products of changes induced by the several steps incidental to their separation, that we are loth to draw any very definite conclusions as to their true chemical composition. By this we do not mean that these three series of products are wholly artificial. Bodies of the general nature of the albumins here indicated unquestionably exist in the corn-kernel. As already stated, an aqueous solution of the corn proteids, entirely freed from globulins, gives a coagulum between 60° and 70°, and another one between 85° and 100°, thus implying the presence of two distinct bodies. It may possibly be assumed that the albumin precipitated by salt and acid is simply a portion of the albumin separated later by coagulation; that this partial precipitation is simply another illustration of the incompleteness characteristic of the separation of these albumins, as witnessed, for example, in the gradual and incomplete coagulation of the above albumin by heat; and further, that the difference in chemical composition between the first and second series of products is simply due to their alteration by the processes made use of. Yet we can hardly consider this the true view. The peculiar heat-coagulation phenomena of the original aqueous solution, before any separations were attempted, lend favor to the view that at least two coagulable albumins are present. On the other hand, the incompleteness of the coagulation at any one point—the fact that more and more coagulum continues to form as the boiling is continued—points clearly to gradual changes, which, doubtless, leave their impression upon the products separated. Thus, in Preparation C, the two albumins coagulated by heat, C^2 1st and C^2 2d, should theoretically have the same composition, the only tangible difference being that the second coagulum required longer heating to bring about its separation, and yet it differs from its neighbor by 1.5 per cent. of nitrogen. Observations of this character, and others which we will not take space to detail, confirm us in the opinion that these soluble bodies are exceedingly prone to change, and doubtless the composition here given is only an approximation to the true make-up of the substances as they exist in the corn-kernel. At the same time, it may not be amiss to recall the fact that in the seed itself, in its various stages of growth and development, kindred changes are doubtless taking place among its natural proteid constituents. Whether the proteose separated by the above methods exists as such in the corn-kernel, or whether it is derived from the other proteids by the methods of separation, is likewise uncertain. A portion of it is unquestionably formed by the hydrolytic changes incidental to the separation of the coagulable proteids, and this favors the view that it is wholly an artificial product.

Further, a similar proteose-like body was directly prepared by heating to 80° C. one of the preceding globulins, dissolved in salt-solution. Again, the somewhat variable composition of the proteoses analysed suggests a mixture of two or more dissimilar proteoses, such as might be expected in an artificial production of the character indicated.

One point to be noted in connection with the proteose is its relatively low content of carbon; a point which is characteristic of most of the albumoses or proteoses formed by the action of the digestive ferments, both from animal and vegetable proteids.

III.—PROTEID MATTER SOLUBLE IN ALCOHOL, BUT INSOLUBLE IN WATER AND SALT-SOLUTIONS.

Under this head we have to deal with only one substance, viz. *Zein* or the "maize fibrin" of Ritthausen. The former name, originally given by Gorham[1] to this peculiar proteid found by him in *Zea mays*, seems especially appropriate, and we would suggest its adoption as a more fitting name than the term employed by Ritthausen. This body, as is well known, is especially characterised by its solubility in weak alcohol, and can be obtained by direct extraction of corn meal with 95-per cent. alcohol, preferably at 40°–60°C., or by extraction of the meal with warm alcohol after previous treatment with water, salt-solution, or both.

Several preparations were made under varying conditions as follows:

Preparation A.

2.5 kilos. of finely ground corn meal were first thoroughly extracted with cold water, after which the residue of meal was treated with 95-per cent. alcohol in sufficient quantity to have the water retained by the meal reduce the strength to about 75 per cent. The mixture was warmed for some hours at about 46° C., and finally filtered at approximately that temperature. The filtrate was concentrated on the water-bath at a temperature below 65° C. The residue of meal was again treated with 75-per cent. alcohol (4 litres) at 60°C. for several hours, and filtered while at that temperature. In all, five successive extractions were made after this fashion, the individual alcoholic extracts being evaporated separately, all at a low temperature. The last three extracts left but little residue on evaporation. As the first two extracts became concentrated the proteid separated as a tough, leathery, yellow-colored mass on the sides and bottom of the dish. It was cut up into small pieces and soaked for several days in cold absolute alcohol. On this first treatment of the proteid with absolute alcohol some little dissolved, presumably from dilution of the alcohol with the water contained in the substance. This alcoholic extract was therefore concentrated to a syrup and the proteid precipitated by ether. It then had the appearance of a crumbly, pulverisable substance, and was easily ground to a powder under absolute alcohol. On slightly warming the alcohol, however, the substance melted and finally dissolved completely in the alcoholic fluid. On cooling this solution, the substance separated in a very gummy state.

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[1] See Berzelius, Jahresbericht 2, (1822), p. 124.

The main portion of the proteid, which had been treated once with absolute alcohol, was treated with successive portions of cold absolute alcohol, as long as anything was dissolved by this reagent, after which it was treated with a mixture of one part of ether and two parts of absolute alcohol and, finally, was soaked in ether alone. After this treatment we were able to reduce it to a fine powder, when it was thoroughly extracted with ether for the complete removal of any adhering fat.

So prepared, the substance was only partially soluble in warm 75-per cent. alcohol, a portion of it during the foregoing process having been converted into an insoluble modification. This change from the soluble (in warm alcohol) to the insoluble form is liable to occur whenever the substance is heated with too watery alcohol, especially if the temperature approaches 100° C., or if the heating be long-continued. The soluble portion referred to above was therefore completely separated by repeated treatment with warm and with boiling dilute alcohol, and the insoluble portion ultimately washed with absolute alcohol and ether and dried at 110° C. for analysis.

The alcoholic solution of the soluble portion of the proteid was poured into about three volumes of water, by which the substance was precipitated in white flocks, which, however, soon commenced to unite and rise to the surface, eventually forming a dense cake. On heating this mass it continued to contract, squeezing out the water in large quantities. The substance, still containing considerable water, was next dissolved in warm 95-per cent. alcohol, the solution filtered, concentrated to about 400 cc. and again poured into a large volume of water, about 3 litres. This time the substance did not separate as before, but remained suspended in the form of a thick emulsion and was made to flock only on the addition of a little salt. It was then filtered off, washed with water until free from chlorides, lastly with alcohol and ether and dried at 110° C. for analysis.

Analysis of Zein. Preparation A.—Soluble.

I. 0.3079 gram substance gave 0.2045 gram $H_2O = 7.34$ per cent. H, and 0.6226 gram $CO_2 = 55.14$ per cent. C.

II. 0.3453 gram substance gave 46.8 cc. N at 17.0° C. and 757.9 mm. pressure $= 15.98$ per cent. N.

III. 0.5310 gram substance fused with $KOH + KNO_3$ gave 0.0197 gram $BaSO_4 = 0.51$ per cent. S.

IV. 1.0210 grams substance fused with $KOH + KNO_3$ gave 0.0402 gram $BaSO_4 = 0.54$ per cent. S.

V. 1.0600 grams substance gave 0.0024 gram ash $= 0.22$ per cent.

VI. 1.0045 grams substance gave 0.0028 gram ash $= 0.27$ per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	55.27	..	..	..	55.27
H	7.35	..	..	..	7.35
N	..	16.01	..	..	16.01
S	..	..	0.51	0.54	0.53
O	..	..	..	..	20.84
					100.00

Analysis of Zein. Preparation A.—Insoluble.

I. 0.3210 gram substance gave 0.2094 gram $H_2O = 7.24$ per cent. H, and 0.6451 gram $CO_2 = 54.80$ per cent. C.

II. 0.4055 gram substance gave 0.2680 gram $H_2O = 7.34$ per cent. H, and 0.8170 gram $CO_2 = 54.94$ per cent. C.

III. 0.3171 gram substance gave 43.1 cc. N at 17.1° C. and 761.6 mm. pressure $= 16.10$ per cent. N.

IV. 0.3250 gram substance gave 43.7 cc. N at 16.8° C. and 763.5 mm. pressure $= 15.98$ per cent. N.

V. 0.5000 gram substance fused with $KOH + KNO_3$ gave 0.0221 gram $BaSO_4 = 0.61$ per cent. S.

VI. 0.9834 gram substance gave 0.0018 gram ash $= 0.18$ per cent.

VII. 0.2637 gram substance gave 0.0005 gram ash $= 0.19$ per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	54.90	55.04	..	..	..	54.97
H	7.25	7.35	..	..	..	7.30
N	..	..	16.01	16.13	..	16.07
S	..	..	..	..	0.61	0.61
O	..	..	..	..	..	21.05
						100.00

Preparation B.

2.5 kilos. of finely ground corn, which had been thoroughly extracted with 10-per cent. salt solution, were treated directly with warm 75-per cent. alcohol, until the alcohol ceased to dissolve anything further. The first alcoholic extract, on concentration, yielded the proteid—doubtless on account of the large amount of sodium chloride it contained—as a yellow, granular mass which could be broken quite readily. The residues from the following extracts, however, were of the same general nature as those described under Preparation A. All of the residues from the several extracts were united, washed with distilled water until the salt was entirely removed, then dissolved in warm 80-per cent. alcohol and the solution filtered to remove any insoluble matter present. The solution was next evaporated on a water-bath nearly to dryness and the residue pressed as dry as possible, yielding a yellow, elastic substance which could be pulled like molasses candy, but which was much more elastic and tough. Its elasticity was so great that it could be pulled into sheets several inches square and very thin. After continued kneading under absolute alcohol, it finally became brittle, a considerable portion of it passing into solution at the same time. After thorough extraction with absolute alcohol in this manner, it was soaked for some time in ether and then ground to a coarse powder. Like the preceding preparation, the proteid was now found only partially soluble in dilute alcohol. It was therefore separated into two portions by continued treatment with warm 80-per cent. alcohol, after first moistening the powdered product with a little water. The insoluble portion was washed with absolute alcohol and ether, and dried at 110° C. for analysis.

The alcoholic solution containing the soluble portion of the proteid was poured into three volumes of water, by which the zein was precipitated in white flocks, which gradually formed into a cake floating on the surface of the fluid. This was redissolved in 95-per cent. alcohol, and again precipitated as before. After a third precipitation in this manner, the substance was dissolved in 95-per cent. alcohol, the solution filtered, and the filtrate evaporated on the water-bath. Towards the end, absolute alcohol was added several times in order to prevent the substance from separating in consequence of the alcohol becoming too dilute. The evaporation was finally carried to dryness, and the residue cut up into small pieces and thoroughly extracted with ether. A portion of this soluble zein, dried at 110° C. until of constant weight, was analysed with the following results:

Analysis of Zein. Preparation B.—Soluble.

I. 0.3252 gram substance gave 0.2132 gram $H_2O = 7.28$ per cent. H, and 0.6550 gram $CO_2 = 54.92$ per cent. C.

II. 0.2968 gram substance gave 0.1932 gram $H_2O = 7.24$ per cent. H, and 0.5985 gram $CO_2 = 54.98$ per cent. C.

III. 0.4193 gram substance gave 57.4 cc. N at 17.3° C. and 755.1 mm. pressure = 16.06 per cent. N.

IV. 0.3569 gram substance gave 49.5 cc. N at 18.4° C. and 755.1 mm. pressure = 16.20 per cent. N.

V. 0.5365 gram substance gave 0.0025 gram ash = 0.46 per cent.

VI. 0.4590 gram substance gave 0.0020 gram ash = 0.46 per cent.

VII. 1.0270 grams substance fused with $KOH + KNO_3$ gave 0.0423 gram $BaSO_4 = 0.57$ per cent. S.

VIII. 1.0093 grams substance fused with $KOH + KNO_3$ gave 0.0385 gram $BaSO_4 = 0.52$ per cent. S.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.17	55.23	..	..	..	..	55.20
H	7.31	7.27	..	..	..	..	7.29
N	..	..	16.13	16.27	..	..	16.20
S	..	..	..	..	0.57	0.52	0.55
O	..	..	..	..	..	..	20.76
							100.00

The insoluble portion, after being dried at 110° C., gave the following results on analysis:

Analysis of Zein. Preparation B.—Insoluble.

I. 0.3562 gram substance gave 0.2290 gram $H_2O = 7.14$ per cent. H, and 0.7200 gram $CO_2 = 55.12$ per cent. C.

II. 0.4284 gram substance gave 0.2772 gram $H_2O = 7.19$ per cent. H, and 0.8660 gram $CO_2 = 55.12$ per cent. C.

III. 0.4203 gram substance gave 0.2708 gram $H_2O = 7.15$ per cent. H, and 0.8504 gram $CO_2 = 55.17$ per cent. C.

IV. 0.3733 gram substance gave 51.2 cc. N at 17.5° C. and 762.4 mm. pressure = 16.24 per cent. N.

V. 0.4449 gram substance gave 60.8 cc. N at 16.9° C. and 761.8 mm. pressure = 16.20 per cent. N.

VI. 0.5238 gram substance fused with $KOH + KNO_3$ gave 0.0245 gram $BaSO_4 = 0.64$ per cent. S.

VII. 0.7747 gram substance fused with $KOH + KNO_3$ gave 0.0350 gram $BaSO_4 = 0.62$ per cent. S.

VIII. 0.4675 gram substance gave 0.0021 gram ash = 0.45 per cent.

IX. 0.4705 gram substance gave 0.0020 gram ash = 0.43 per cent.

Percentage Composition of the Ash-free Substance.

								Average.
C	55.36	55.36	55.41	..	..	..	..	55.37
H	7.17	7.22	7.18	..	..	..	..	7.19
N	..	..	..	16.31	16.27	..	..	16.29
S	..	..	..	..	..	0.64	0.62	0.63
O	..	..	..	..	..	..	..	20.52
								100.00

Preparation C.

2.5 kilos. of corn meal, previously extracted with 5-per cent. ammonium chloride solution, were treated several times with warm 75-per cent. alcohol, and the alcoholic extract concentrated at a low temperature. The leathery-like residues left by evaporation of the alcohol were washed somewhat with water, then dissolved, so far as possible, in warm 80-per cent. alcohol, the clear fluid evaporated nearly to dryness, and the residue digested repeatedly with absolute alcohol and, lastly, with ether. On becoming air-dry, the substance was pulverised and again extracted with ether. It was then dissolved as completely as possible in 80-per cent. alcohol, after having been first gently warmed with a little water. A considerable quantity of the substance remaining insoluble, this was removed by decantation and filtration, the residue washed first with dilute alcohol, lastly with alcohol and ether, and dried at 110° C. for analysis. The alcoholic solution containing the soluble portion of the proteid was precipitated by being poured into water, a process which was repeated three times; after which the precipitated zein was digested with absolute alcohol and finally with ether, and a portion dried at 110° C. for analysis.

Analysis of Zein. Preparation C.—Soluble.

I. 0.3728 gram substance gave 0.2396 gram $H_2O = 7.14$ per cent. H, and 0.7520 gram $CO_2 = 55.01$ per cent. C.

II. 0.3587 gram substance gave 0.2305 gram $H_2O = 7.14$ per cent. H, and 0.7236 gram $CO_2 = 55.01$ per cent. C.

III. 0.4218 gram substance gave 58.0 cc. N at 17.2° C. and 759.6 mm. pressure = 16.24 per cent. N.

IV. 0.4085 gram substance gave 55.9 cc. N at 17.2° C. and 760.2 mm. pressure = 16.17 per cent. N.

V. 1.0375 grams substance fused with KOH + KNO_3 gave 0.0460 gram $BaSO_4$ = 0.61 per cent. S.

VI. 0.8267 gram substance fused with KOH + KNO_3 gave 0.0348 gram $BaSO_4$ = 0.58 per cent. S.

VII. 0.4610 gram substance gave 0.0008 gram ash = 0.17 per cent.

VIII. 0.5250 gram substance gave 0.0009 gram ash = 0.17 per cent.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.10	55.10	..	..	..	..	55.10
H	7.15	7.15	..	..	..	..	7.15
N	..	..	16.26	16.19	..	..	16.22
S	..	..	..	..	0.61	0.58	0.60
O	..	..	..	..	..	..	20.93
							100.00

Analysis of Zein, Preparation C.—Insoluble.

I. 0.3885 gram substance gave 0.2518 gram H_2O = 7.20 per cent. H, and 0.7835 gram CO_2 = 54.99 per cent. C.

II. 0.3848 gram substance gave 0.2514 gram H_2O = 7.25 per cent. H, and 54.94 per cent. C.

III. 0.4964 gram substance gave 67.9 cc. N at 17.5° C. and 763.6 mm. pressure = 16.22 per cent. N.

IV. 0.4119 gram substance gave 57.0 cc. N at 17.7° C. and 760.6 mm. pressure = 16.33 per cent. N.

V. 0.5295 gram substance fused with KOH + KNO_3 gave 0.0240 gram $BaSO_4$ = 0.62 per cent. S.

VI. 0.5890 gram substance fused with KOH + KNO_3 gave 0.0273 gram $BaSO_4$ = 0.64 per cent. S.

VII. 0.5250 gram substance gave 0.0014 gram ash = 0.27 per cent.

VIII. 0.5737 gram substance gave 0.0013 gram ash = 0.23 per cent.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.12	55.07	..	..	..	..	55.10
H	7.21	7.26	..	..	..	..	7.23
N	..	..	16.26	16.37	..	..	16.31
S	..	..	..	..	0.62	0.64	0.63
O	..	..	..	..	..	..	20.93
							100.00

Preparation D.

3.0 kilos. of freshly ground corn were extracted directly with about 4 litres of 75-per cent. alcohol for 24 hours, at a temperature varying between 40° and 60° C., and filtered while warm. The clear extract was then concentrated to about 500 cc. and the proteid precipitated by pouring the solution into a large volume of water. The substance so separated, in the form of lumps and strings, was washed frequently with a large amount of water, and finally soaked in water for some hours. It was then collected on muslin, squeezed dry, treated with 95-per cent. alcohol, in which it dissolved readily and almost completely, and again precipitated by water. This process of solution in dilute alcohol and reprecipitation with water was repeated several times, the product ultimately being divided into two fractions, which differed from each other simply in the number of times this process had been repeated. The two products, D^1 and D^2, were then treated repeatedly with absolute alcohol and ether, until all coloring matter and fat had been removed, after which they were ground to a fine powder and portions dried at 110° C. for analysis.

The residue of meal, extracted a second time with warm dilute alcohol, yielded a second portion of zein, which was separated and purified in essentially the same manner as the preceding preparation, the final product being wholly soluble in dilute alcohol. This was likewise reduced to a powder, after successive treatment with ether and absolute alcohol, and a portion dried at 110° C. for analysis. (Product D^3.)

Analysis of Zein. Preparation D^1.

I. 0.3028 gram substance gave 0.1991 gram $H_2O = 7.30$ per cent. H, and 0.6107 gram $CO_2 = 54.99$ per cent. C.

II. 0.2455 gram substance gave 0.1590 gram $H_2O = 7.20$ per cent. H, and 0.4952 gram $CO_2 = 55.00$ per cent. C.

III. 0.3580 gram substance gave 47.8 cc. N at 16.8° C. and 766.2 mm. pressure = 15.92 per cent. N.

IV. 0.3557 gram substance gave 48.3 cc. N at 18.4° C. and 756.3 mm. pressure = 15.90 per cent. N.

V. 0.5000 gram substance fused with $KOH + KNO_3$ gave 0.0234 gram $BaSO_4 = 0.64$ per cent. S.

VI. 0.5145 gram substance gave 0.0040 gram ash = 0.78 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	55.42	55.43	..	..	..	55.42
H	7.35	7.25	..	..	..	7.30
N	..	..	16.04	16.02	..	16.03
S	..	..	..	..	0.64	0.64
O	..	..	..	..	..	20.61
						100.00

Analysis of Zein. Preparation D^2.

I. 0.3401 gram substance gave 0.2220 gram $H_2O = 7.25$ per cent. H, and 0.6857 gram $CO_2 = 54.98$ per cent. C.

II. 0.3333 gram substance gave 0.2156 gram $H_2O = 7.19$ per cent. H, and 0.6740 gram $CO_2 = 55.14$ per cent. C.

III. 0.3696 gram substance gave 50.1 cc. N at 17.0° C. and 757.4 mm. pressure = 15.97 per cent. N.

IV. 0.3731 gram substance gave 50.5 cc. N at 17.9° C. and 755.7 mm. pressure = 15.89 per cent. N.

V. 0.6198 gram substance fused with $KOH + KNO_3$ gave 0.0305 gram $BaSO_4 = 0.67$ per cent. S.

VI. 0.5065 gram substance gave 0.0030 gram ash = 0.59 per cent.

VII. 0.5131 gram substance gave 0.0035 gram ash = 0.68 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	55.33	55.49	..	..	..	55.41
H	7.29	7.23	..	..	..	7.26
N	..	..	16.07	15.99	..	16.03
S	..	..	..	..	0.67	0.67
O	..	..	..	..	..	20.63
						100.00

Analysis of Zein. Preparation D^3.

I. 0.3638 gram substance gave 0.2366 gram $H_2O = 7.22$ per cent. H, and 0.7300 gram $CO_2 = 54.72$ per cent. C.

II. 0.3892 gram substance gave 0.2551 gram $H_2O = 7.27$ per cent. H, and 0.7846 gram $CO_2 = 54.99$ per cent. C.

III. 0.4819 gram substance gave 65.3 cc. N at 17.9° C. and 761.2 mm. pressure = 15.99 per cent. N.

IV. 0.4143 gram substance gave 55.6 cc. N at 17.0° C. and 759.7 mm. pressure = 15.86 per cent. N.

V. 0.5200 gram substance gave 0.0038 gram ash = 0.73 per cent.

VI. 0.5163 gram substance gave 0.0039 gram ash = 0.75 per cent.

VII. 1.0117 grams substance fused with $KOH + KNO_3$ gave 0.0395 gram $BaSO_4 = 0.54$ per cent. S.

VIII. 1.0520 grams substance fused with $KOH + KNO_3$ gave 0.0425 gram $BaSO_4 = 0.56$ per cent. S.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.12	55.38	..	..	..	..	55.25
H	7.27	7.32	..	..	..	..	7.29
N	..	..	16.10	15.97	..	..	16.04
S	..	..	..	..	0.54	0.56	0.55
O	..	..	..	..	..	..	20.87
							100.00

A comparison of the analyses of these several preparations of zein, or maize fibrin, shows a remarkable uniformity in composition, and furthermore indicates that the insoluble modification of the proteid is not at all different in composition from the main product. This is plainly apparent from the following table:

	Soluble Zein.						*Insoluble Modification.*			
	A	B	C	D¹	D²	D³	A	B	C	Average.
C	55.27	55.20	55.10	55.42	55.41	55.25	54.97	55.37	55.10	55.23
H	7.35	7.29	7.15	7.30	7.26	7.29	7.30	7.19	7.23	7.26
N	16.01	16.20	16.22	16.03	16.03	16.04	16.07	16.29	16.31	16.13
S	0.53	0.55	0.60	0.64	0.67	0.55	0.61	0.63	0.63	0.60
O	20.84	20.76	20.93	20.61	20.63	20 87	21.05	20.52	20.73	20.78
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash	0.24	0.46	0.17	0.78	0.63	0.74	0.19	0.44	0.25	

Maize fibrin, as prepared and analysed by Ritthausen,[1] was found to contain 54.69 per cent. C, 7.51 per cent. H, 16.33 per cent. N and 0.69 per cent. S, thus agreeing very closely with our data, except in carbon. This slight difference in composition obviously cannot be explained with certainty, but considering the great care used in the purification of our products and their close agreement in composition, together with the use of unquestionable analytical methods, it seems probable that the above series of data must accurately represent the true composition of maize fibrin or zein. It is furthermore equally evident from the analytical data that this substance is a homogeneous body, and not composed of two or more dissimilar bodies.

Freshly precipitated zein (precipitated from an alcoholic solution by water) is wholly insoluble in 0.5-per cent. sodium carbonate, even when warmed with the alkaline fluid at 40° C. for 24 hours. It is likewise equally insoluble in 0.2-per cent. hydrochloric acid, but can be completely dissolved by an aqueous solution of potassium hydroxide of 0.2-per cent. strength. So dissolved it is not converted into alkali-albumin, as is indicated by the fact that the precipitate produced on neutralisation of the alkaline fluid is not soluble in excess of dilute acid, but is completely dissolved by alcohol. This resistance of the proteid to the action of alkalies is quite pronounced; thus, exposure of the substance to the action of 0.2-per cent. caustic potash at 40° C. for 24 hours is not followed by any conversion into alkali-albumin. This is likewise true even when the strength of the alkali is raised to 2.0-per cent. KOH. Exposure to a higher temperature than 40° C. with this strength of alkali is, however, followed by a change in the proteid.

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[1] "Ueber den Stickstoffgehalt der Pflanzen-Eiweisskörper."—Pflüger's Archiv für die gesammte Physiologie **18**, 246.

Freshly precipitated zein is wholly insoluble in water, and on being boiled with water is changed into the insoluble modification already referred to, which is insoluble both in alcohol and dilute (0.2-per cent.) potassium hydroxide. Zein gives the usual proteid reactions with Millon's xanthoprotein and biuret tests.

On warming the proteid at 40° C. with pepsin-hydrochloric acid, the substance is gradually dissolved and converted into proteose-like bodies, and true peptones non-precipitable by saturation with ammonium sulphate.

Boiled with dilute sulphuric acid (6 cc. concentrated acid in 300 cc. water) zein at first melts, forming a gummy mass or lump which is only slowly attacked by the acid, the portion dissolved being mainly converted into proteoses and peptone. Heated with stronger sulphuric acid, it undergoes a more pronounced decomposition, yielding large amounts of leucin with considerable tyrosin, and apparently large amounts of glutamic acid.

Corn meal, after thorough extraction with salt-solution and warm dilute alcohol, yields little proteid matter to dilute solutions of potassium hydroxide (0.2-per cent.).

Summary.

1. The maize-kernel contains several distinct proteids, well characterised in reactions and composition. Of these, there are three globulins, one or more albumins, and an alcohol-soluble proteid.

2. The globulin obtainable from the maize-kernel by extraction with 10-per cent. solution of sodium chloride and separation by the usual methods—as by dialysis, or by precipitation with ammonium sulphate, followed by dialysis—is a mixture of two or more dissimilar globulins, differing from each other both in composition and in coagulation-points.

3. The mixed globulin can be approximately separated into its

two constituents by fractional heat-coagulation, or by a process of "recrystallisation" from warm dilute salt-solution. In the former process, there is at the same time formed a small amount of proteose-like bodies, presumably by hydrolysis of the less resistant globulin.

4. The two globulins separable by the above methods from the mixed globulin are a myosin-like body and a vitellin-like body.

The myosin-like globulin is characterised by containing about 16.8 per cent. of nitrogen and 1.2 per cent. of sulphur, agreeing closely in its composition with animal myosin. It has, however, a coagulation-point (in 10-per cent. salt solution) of about 70° C.

The vitellin-like globulin, on the other hand, contains about 18.1 per cent. of nitrogen and 0.85 per cent. of sulphur, agreeing closely with the generally accepted composition of phyto-vitellin. This body, however, is almost entirely non-coagulable by heat when dissolved in dilute salt-solution, except in the presence of acetic acid. It is more soluble in warm salt-solutions than in cold, and when separated from the former by cooling the fluid, or on dialysis, almost invariably appears in the form of small spheroids.

5. These two globulins exist as such in the corn or maize kernel, and are not products of a cleavage of the so-called mixed globulin. This is evident from the coagulation-points of a salt-solution of the mixed globulin; from the fact that the separation can be accomplished without the aid of heat; and, lastly, since it is possible to directly extract the individual globulins from the kernel, by the use of appropriate solvents.

6. Direct extraction of finely powdered corn meal with water yields a dilute salt-solution, which dissolves the myosin-like globulin, leaving the bulk of the vitellin-like substance undissolved. Probably, the character of the salts present in the kernel plays an important part in this separation. From this solution the myosin can be separated in a fair degree of purity by the usual methods.

7. Extraction of corn meal with 10-per cent. salt solution, after previous extraction with water, dissolves the vitellin-like globulin, from which solution it can be separated by the customary methods. So prepared, it agrees exactly with the vitellin separated by heat-coagulation from the mixed globulin.

8. The third globulin present in the maize-kernel is characterised by extreme solubility in very dilute salt-solutions, especially phosphates and sulphates. It separates from such solutions only

by prolonged dialysis—*i. e.* not until nearly every trace of the above salts has been removed. It coagulates (in a 10-per cent. salt solution) in the neighborhood of 62° C., and contains 15.2 per cent. of nitrogen and 1.26 per cent. of sulphur.

9. Through the long-continued action of water, and also of strong solutions of salt, as ammonium sulphate, the myosin-like globulin, and the globulin with a still lower content of nitrogen, are changed into insoluble modifications, soluble, however, in 0.5-per cent. sodium carbonate solution, from which they are precipitated on neutralisation, apparently as albuminates. So prepared, these insoluble modifications are characterised by a relatively high content of carbon.

10. An aqueous extract of corn meal, as well as a sodium-chloride extract, contains, in addition to the globulins, apparently two albumin-like bodies, more or less coagulable by heat, but as prepared, unlike in chemical composition.

11. A certain amount of proteose can be detected in the extracts of corn meal, after the globulins and albumins have been entirely removed, but apparently this is mainly, if not wholly, an artificial product resulting from the hydrolysis of some one or more of the preceding bodies.

12. Especially noteworthy is the presence in the maize-kernel of a peculiar proteid body known as maize fibrin, or better as *zein*, soluble in warm dilute alcohol, but insoluble in water.

Zein is characterised by a high content of carbon, by its resistance to the action of dilute alkalies (*i. e.*, non-convertibility into alkali-albuminate), and by the ease with which it is converted into an insoluble modification on being warmed with water, or with very weak alcohol.

Soluble zein and the insoluble modification have the same chemical composition. Both respond to the ordinary proteid reactions.

Contributions from the Chemical Laboratory of Cornell University.

DECOMPOSITION WITH ALCOHOL OF THE DIAZO COMPOUNDS OBTAINED FROM SOME OF THE NITRO-NAPHTHYL-AMINES.

BY W. R. ORNDORFF AND M. CAUFFMAN.

In a previous paper[1] it was shown that when the α-diazo-naphthalene sulphate is decomposed by alcohol, about 40 per cent. is converted into naphthalene and 23 per cent. into the ethyl ether of α-naphthol. With the β-diazo-naphthalene salts, however, it was found that, when decomposed by alcohol in exactly the same manner, about 30 per cent. was converted into the ethyl ether of β-naphthol, and only 7 per cent. was obtained in the form of naphthalene. From these results it was concluded that in the case of the simple diazo-naphthalene salts, when decomposed by alcohol, the course of the reaction is influenced by the position of the diazo group in the naphthalene molecule. When the diazo group occupies the α-position the tendency is toward the introduction of hydrogen according to the well known equation:

$$C_{10}H_7.N_2.HSO_4 + C_2H_6O = C_{10}H_8 + C_2H_4O + N_2 + H_2SO_4.$$

When, however, the diazo group is removed to the β-position the reaction proceeds in a different manner; the tendency here is towards the introduction of the ethoxy group in place of the diazo group as shown in the equation:

$$C_{10}H_7.N_2.HSO_4 + HO.C_2H_5 = C_{10}H_7OC_2H_5 + N_2 + H_2SO_4.$$

Remsen and his pupils have shown that in the case of the substituted diazo-benzene salts, not only the position of the diazo group in the molecule with reference to other groups, but the character of the substituting group or atoms exerts an influence on the course of the reaction, when these compounds are decomposed by alcohol. Thus while the diazo-benzene salts themselves, when decomposed by alcohol, were found to yield principally phenol ethers, the nitro-diazo-benzene salts made from the ortho-, meta- and para-nitranilines gave only nitro-benzene. The influence of the nitro group on the course of the reaction is plainly shown here. The diazo group is replaced by hydrogen in each case, and it seems to make no difference whether the nitro group occupies the ortho, meta, or para position with reference to the diazo group.

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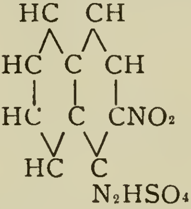
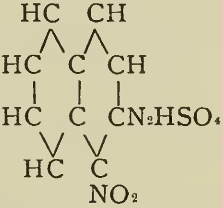
[1] This Journal **13**, 153.

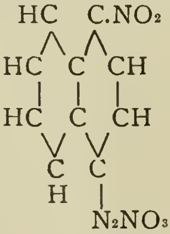
The study of the decomposition by alcohol of the nitro-diazo-naphthalene salts obtained from the nitro-naphthyl-amines was undertaken in order to determine if the influence of the nitro group was the same in the naphthalene as in the benzene series. Moreover, it is possible in the naphthalene series to obtain two compounds, in which the position of the nitro group with reference to the diazo group does not change, although the diazo group is first in the α-, and then in the β-position. Thus β_2-nitro-α_2-diazo-naphthalene sulphate, represented graphically by the following formula,



may be readily made, and also α_2-nitro-β_2-diazo-naphthalene sulphate,



In these two subtances it will be seen, that though in the first case the diazo group is in the α-position, and in the second in the β-, the nitro group in both cases is in the ortho position with reference to the diazo group. By decomposing these two compounds with alcohol it was hoped the influence of the nitro group could be determined irrespective of the position it occupied in the molecule with reference to the diazo group. Incidentally the decomposition of α_1-nitro-α_2-diazo-naphthalene nitrate,



by alcohol was studied for the sake of completeness, and in order to show the influence, if any, of the position of the nitro group on the course of the reaction. In designating the position of the groups in the naphthalene molecule, reference is made to the formula on page 134, volume II., of Beilstein's "Handbuch der organischen Chemie."

Preparation of the $\beta_2\alpha_2$-nitro-naphthyl-amine and of the $\alpha_1\alpha_2$-nitro-naphthyl-amine.—The $\beta_2\alpha_2$-nitro-naphthyl-amine and the $\alpha_1\alpha_2$-nitro-naphthyl-amine were made together. For this purpose α-naphthyl-amine was converted into the acet-naphthalide according to the directions of Liebermann,[1] and the acet-compound purified by recrystallisation from hot water. The product obtained was pure and melted at 159°. The $\beta_2\alpha_2$- and the $\alpha_1\alpha_2$-nitro-acet-naphthalide were then made by dissolving the acet-compound in glacial acetic acid, adding fuming nitric acid and allowing the mixture to stand. The two products crystallised out together. These were filtered off, and from the mother-liquor on standing, some of the pure $\alpha_1\alpha_2$-nitro-acet-naphthalide afterwards crystallised out. Since the two nitro compounds crystallised out together and gave a product melting at 171°, which it was impossible to separate into its constituents by fractional crystallisation, the method recommended by Lellmann and Remy[2] was tried. The double compound was treated with about sixty per cent. of the theoretical amount of caustic potash necessary to saponify. The $\alpha_1\alpha_2$-product under these conditions is saponified, the $\beta_2\alpha_2$-nitro-acet-naphthalide remaining unchanged. The $\alpha_1\alpha_2$-nitro-naphthyl-amine was separated from the $\beta_2\alpha_2$-nitro-acet-naphthalide by the second method recommended by Lellmann and Remy[2], and both substances were purified by recrystallisation from alcohol. The $\beta_2\alpha_2$-nitro-acet-naphthalide was then saponified in alcoholic solution with concentrated hydrochloric acid, and the product recrystallised from alcohol. The $\beta_2\alpha_2$-nitro-naphthyl-amine melted at 144°, while the $\alpha_1\alpha_2$-product melted at 191°.

Preparation of the β_2-nitro-α_2-diazo-naphthalene sulphate.—The $\beta_2\alpha_2$-nitro-naphthyl-amine was dissolved in a small amount of ordinary alcohol, an excess of concentrated sulphuric acid gradually added, and, after cooling, a little more than the theoretical amount of amyl nitrite was added. The diazo compound was then crystallised out of the solution by the addition of ether, and cooling in a freezing-mixture. The diazo sulphate was then filtered off, and on the addition of more ether to the filtrate and cooling, a further crop of crystals of the diazo sulphate was obtained.

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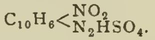
[1] Ann Chem. (Liebig) **183**, 229.

[2] Ber. d. chem. Ges. **20**, 892.

Several attempts were made to obtain the nitro-diazo-naphthalene nitrate, but without success, and as the supply of the $\beta_2\alpha_2$-nitro-naphthyl-amine was small, the attempt was abandoned.

The β_2-nitro-α_2-diazo-naphthalene sulphate was washed with absolute alcohol and dry ether, carefully dried in the dark under sulphuric acid, and subjected to an analysis. For this purpose the diazo salt was decomposed in the usual way in water, the nitrogen evolved, collected and measured, and the acid titrated with a standard alkali solution. The following results were obtained:

I. 0.0587 gram gave 4.9 cc. nitrogen at 23° and 742 mm. bar.
I. 0.0587 gram gave 0.01566 gram sulphur trioxide.
II. 0.0905 gram gave 7.8 cc. nitrogen at 23° and 742 mm. bar.
II. 0.0905 gram gave 0.0246 gram sulphur trioxide.

	Calculated for  $C_{10}H_6<\begin{smallmatrix}NO_2\\N_2HSO_4\end{smallmatrix}$.	Found.	
		I.	II.
N_2	9.42	9.19	9.47
SO_3	26.93	26.68	27.18

Properties of the β_2-nitro-α_2-diazo-naphthalene sulphate.—The β_2-nitro-α_2-diazo-naphthalene sulphate thus prepared crystallises in yellow needles, which are insoluble in ether and absolute alcohol, but soluble in water and dilute alcohol. When heated with water, decomposition takes place, nitrogen is evolved, and β_2-nitro-α_2-naphthol results. Heated alone it explodes feebly, but does not decompose on percussion. The salt decomposes when left exposed to the light and air, the crystals becoming finally red in color. An examination of the crystals was kindly made by Professor Kemp, formerly of the Geological Department of Cornell University, and now of Columbia College, who reported as follows: "The felty substance is shown under the microscope to consist of a mass of small acicular crystals of a strong lemon-yellow color. They average about one-fortieth of a millimeter in diameter and are several times as long. They seem to have an hexagonal cross-section and to form slender hexagonal prisms. No terminations could be detected, as their ends were broken. Pleochroism is present, yellow to lighter yellow; the lighter tint appearing in the ray vibrating parallel to the long axis of the prism. With crossed nicols the needles extinguish, in some cases parallel, in others at about 7° to 10°, and in others from 18° to 25°. This variation doubtless corresponded to the different portions that were uppermost. They indicate that the crystals are either monoclinic or triclinic. The parallel extinction makes the probability of their being monoclinic greater than triclinic, although the possibility of an inclined extinction of the latter being very near parallelism cannot be overlooked. They polarise in brilliant colors, and have a quite high refractive index. On exposure to the air the color of the needles changes in a few days to an orange tint, and then to an opaque brick-red."

Decomposition of the β_2-nitro-α_2-diazo-naphthalene sulphate in alcohol.—The method given by Lellmann[1] was made use of, and the diazo compound was not isolated. The $\beta_2\alpha_2$-nitro-naphthylamine was dissolved in just enough alcohol to prevent its precipitating out on cooling, an excess of concentrated sulphuric acid was added, the mixture cooled, and a large excess of ethyl nitrite in alcohol added. As long as the mixture was kept cool, no change took place, but as soon as it acquired the temperature of the room, nitrogen was given off freely, and the odor of aldehyde was quite marked. The reaction was completed by warming on the water-bath. Water was added to the red-colored fluid while hot and a substance crystallised out. This was allowed to settle, and was then filtered off, and the filtrate examined, but was found to contain nothing but sulphuric acid and some tar. The precipitate was then dissolved in dilute alcohol and recrystallised fractionally, and the melting-point of each fraction determined in order to detect the presence of a second substance. The melting-point, however, remained constant at about 76°–79°, the variation being due to the presence of a small amount of tarry matter. The crystals, besides showing the same melting-point as β-nitro-naphthalene, exhibited the same solubility in alcohol and the same crystal form under the microscope, and on analysis gave the following results:

0.5028 gram gave 0.0495 gram ammonia by the modified Kjeldahl method.

	Calculated for $C_{10}H_7NO_2$.	Found.
N	8.9 per cent.	8.10 per cent.

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[1] Ber. d. chem. Ges. **19**, 236.

The other substance which we would naturally expect to get here, would be the ethyl ether of β_2-nitro-α_2-naphthol. This is not known, but as the β_2-nitro-α_2-naphthol itself melts at 128°, it seems fair to suppose that the presence of even a small quantity of the ethyl ether of β_2-nitro-α_2-naphthol would have shown itself by raising the melting-point of the crystals. The only change noted, however, was a slight *lowering* of the melting-point, and this was probably due to the presence of a small amount of tar. The only product of the decomposition of β_2-nitro-α_2-diazo-naphthalene sulphate in alcohol, therefore, is β-nitro-naphthalene. *The hydrogen reaction alone takes place in this case.* From 4.17 grams of the β_2-nitro-α_2-naphthylamine taken, 3.23 grams of β-nitro-naphthalene were obtained, which corresponds to a conversion of about 84 per cent. of the diazo compound into β-nitro-naphthalene. Attention should be called here to the fact that when α-diazo-naphthalene sulphate itself was decomposed in alcohol, 40 per cent. was converted into naphthalene, and 23 per cent. into the ethyl ether of α-naphthol.

Preparation of the α_2-nitro-β_2-naphthylamine.—The directions of Liebermann and Jacobson,[1] slightly modified by Merz and Weith,[2] were followed closely in the preparation of this substance. β-Naphthylamine was heated with glacial acetic acid, and thus converted into the acet-compound, which was recrystallised from alcohol. The nitro group was then introduced by dissolving the acet-compound in glacial acetic acid and adding fuming nitric acid. This, when recrystallised from alcohol, was found to have the melting-point 123°. The α_2-nitro-β_2-acet compound was then saponified in alcoholic solution with caustic potash, and the nitro-naphthyl-amine precipitated by adding water. On recrystallising from alcohol the crystals were found to melt sharply at 126°–127°.

Preparation of the α_2-nitro-β_2-diazo-naphthalene sulphate.—The method pursued in preparing the α_2-nitro-β_2-diazo-naphthalene sulphate was the same that was used in the preparation of the β_2-nitro-α_2-diazo-naphthalene sulphate. The nitro-naphthyl-amine was dissolved in sufficient hot alcohol to prevent its precipitating out on cooling; an excess of concentrated sulphuric acid was gradually added to the well-cooled solution, and then, keeping the solution in ice water, a little more than the theoretical amount of amyl nitrite was added. The color of the solution changed from light to dark red, and on adding ether and cooling in a freezing-

[1] Ann. Chem. (Liebig) **211**, 45.

[2] Ber. d. chem. Ges. **14**, 2343.

mixture, the α_2-nitro-β_2-diazo-naphthalene sulphate crystallised out after standing a short time. The mother-liquor was then treated with more ether, again cooled in a freezing-mixture, when more of the diazo compound crystallised out.

From 15 grams of the α_2-nitro-β_2-naphthyl-amine about 17 grams of the diazo compound were obtained, which is about 72 per cent. of the theoretical amount. The diazo salt was then washed with absolute alcohol and ether, dried in the dark, and analysed by decomposing in water, collecting and measuring the nitrogen evolved and titrating the sulphuric acid with a standard alkali solution. The following results were obtained:

In the determination of nitrogen—

I. 0.0811 gram gave 6.4 cc. nitrogen at 21° and 747 mm. bar.

II. 0.0545 gram gave 4.5 cc. nitrogen at 22° and 746 mm. bar.

For sulphuric acid—

I. 0.8811 gram gave 0.02186 gram sulphur trioxide.

II. 0.0545 gram gave 0.01493 gram sulphur trioxide.

	Calculated for $C_{10}H_6<\substack{NO_2\\N_2HSO_4}$.	Found. I.	II.
N_2	9.42 per cent.	8.82	9.17
SO_3	26.93 "	26.95	27.39

Properties of α_2-nitro-β_2-diazo-naphthalene sulphate.—The α_2-nitro-β_2-diazo-naphthalene sulphate crystallises in orange-yellow needles which, though readily soluble in water and dilute alcohol, are difficultly soluble in absolute alcohol and insoluble in anhydrous ether. When heated with water, nitrogen is evolved and α_2-nitro-β_2-naphthol results; when heated alone, the substance explodes feebly at 167° but does not explode on percussion. The diazo salt undergoes decomposition when left exposed to the light and air, the color finally becoming brown. When protected from the action of the light, the crystals lost their color very slowly, and a change was barely perceptible after the lapse of several days.

Decomposition of the α_2-nitro-β_2-diazo-naphthalene sulphate in alcohol.—The α_2-nitro-β_2-diazo-naphthalene sulphate was decomposed in absolute alcohol according to the method already described.[1] The odor of aldehyde was perceptible throughout the experiment. The contents of the flask were then filtered to remove a small amount of tar, and the excess of alcohol distilled

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[1] This Journal **13**, 156.

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off on the water-bath. This alcoholic distillate smelled strongly of aldehyde. A large quantity of water was then added to the flask and the whole subjected to distillation in steam. A light yellow substance distilled with the steam. When the solid ceased to distil with the steam, the operation was discontinued, and the non-volatile residue remaining in the flask was examined.

The residue.—This consisted of water containing sulphuric acid and a tarry substance. The tar was filtered off, the acid neutralised, and the solution slowly evaporated, but besides the sulphate and a small amount of tar, nothing else was detected. The tar was now dissolved in alcohol and the solution divided into two portions, one of which was precipitated with water, adding a little at a time and allowing to settle and then filtering; the second was decolorised by boiling with bone-black and allowed to evaporate spontaneously. From the first solution a few crystals were obtained, melting at 58° and possessing other properties which proved them to be α-nitro-naphthalene. From the second only tarry matter could be separated.

The distillate.—The contents of the receiver were allowed to settle over night, then filtered and the precipitate dried. This precipitate was then dissolved in alcohol and subjected to fractional crystallisation. The melting-point of the various fractions remained constant at about 58°. Only the last portions varied one or two degrees from this point, melting at 56°, and this was shown to be due to traces of tar present in the crystals. The crystals melted at 58°, the melting-point of α-nitro-naphthalene, possessed the same solubility in alcohol, and same crystal form under the microscope. On reduction with iron and acetic acid they gave α-naphthyl-amine, characterised by its peculiar and unpleasant odor, and melting-point of 50°. A determination of the nitrogen in the nitro product by the modified Kjeldahl method gave the following results:

0.7041 gram gave 0.0709 gram ammonia.

	Calculated for $C_{10}H_7NO_2$.	Found.
N	8.09	8.28

The substance is undoubtedly α-nitro-naphthalene. The ethyl ether of α_2-nitro-β_2-naphthol, which we would expect here as one of the products of the decomposition of the diazo compound in alcohol, melts at 103°–104°, and if any of this substance had been present the melting-point would not have remained constant. The only product therefore of the decomposition of the α_2-nitro-β_2-diazo-naphthalene sulphate in alcohol is α-nitro-naphthalene. *The hydrogen reaction alone takes place here.* From 8.1 grams of the diazo compound 2.45 grams of the nitro-naphthalene were obtained, which corresponds to a conversion of about 52 per cent. of the diazo compound into α-nitro-naphthalene. It should be remembered in this connection that when β-diazo-naphthalene sulphate itself was decomposed in alcohol, 30 per cent. was converted into the ethyl ether of β-naphthol and only 7 per cent. into naphthalene.

Preparation of the α_2-nitro-β_2-diazo-naphthalene nitrate.—The α_2-nitro-β_2-naphthyl-amine was dissolved in a small quantity of alcohol, the solution cooled, and then an excess of concentrated nitric acid gradually added. The nitrate thus prepared was diazotised by cooling the solution and adding gradually a little more than the theoretical amount of amyl nitrite. The solution turned dark-red and gave yellow crystals of the α_2-nitro-β_2-diazo-naphthalene nitrate on adding ether and cooling. An analysis of the diazo nitrate by the usual method gave the following results:

0.0365 gram gave 3.6 cc. nitrogen at 21° and 742 mm. bar.
0.0365 gram gave 0.0085 gram NO_3.

	Calculated for $C_{10}H_6<^{NO_2}_{N_2.NO_3}$.	Found.
N_2	10.68	10.97
NO_3	23.66	23.28

Properties of the α_2-nitro-β_2-diazo-nitrate.—The diazo salt is soluble in water and dilute alcohol, inscluble in ether which is free from water. It crystallises in light-yellow colored needles which rapidly turn dark brown when exposed to the light. It explodes on heating, but not by percussion. The decomposition with water and alcohol gave the same products that were obtained with the diazo sulphate.

Preparation of α_1-nitro-α_2-diazo-naphthalene nitrate.—The α_1-nitro-α_2-diazo-naphthalene nitrate was made by adding just enough absolute alcohol to the α_1-nitro-α_2-naphthyl-amine to form a thin paste; this was then treated with an excess of dilute nitric acid, and a little more than the theoretical amount of amyl nitrite slowly added until everything went into solution. The diazo compound was then precipitated out with ether in the cold.

Several other methods were tried, but this one yielded the most satisfactory results. Many attempts were made to obtain the diazo sulphate, but without success. In all cases the sulphate failed to crystallise out, and a red dye-stuff, which turned blue on treatment with sulphuric acid, was obtained instead. This dye-stuff corresponds to the diazo-amido compound, $C_{20}H_{13}N_5O_4$, obtained by Liebermann[1] under similar circumstances from α_1-nitro-α_2-naphthylamine.

The yellow needles of the diazo nitrate were filtered off, washed as usual with absolute alcohol and anhydrous ether, and dried in the dark. An analysis gave the following results :

In the determination of nitrogen—

I. 0.0327 gram gave 3.1 cc. nitrogen at 23° and 742 mm. bar.

II. 0.2320 gram gave 21.4 cc. nitrogen at 22° and 740 mm. bar.

For nitric acid—

0.2320 gram gave 0.0539 gram NO_3.

	Calculated for $C_{10}H_6<^{NO_2}_{N_2NO_3}$.	Found. I.	Found. II.
N_2	10.68	10.37	10.16
NO_3	23.66	...	23.23

Properties of α_1-nitro-α_2-diazo-naphthalenenitrate.—The α_1-nitro-α_2-diazo-naphthalene nitrate crystallises in light-yellow colored needles, which turn to a greenish yellow on short exposure to the light. It is readily soluble in water, moderately so in alcohol, and insoluble in anhydrous ether. It explodes feebly on ignition but not by percussion. Under the microscope the crystals appear as prisms of a deep yellow color.

Decomposition of the α_1-nitro-α_2-diazo-naphthalene nitrate in alcohol.—The method of Liebermann[2] was followed here, and the diazo compound was not isolated. Nitrogen trioxide, generated in the usual way from arsenic trioxide and nitric acid, was conducted into a well-cooled pasty mixture of α_1-nitro-α_2-naphthylamine and dilute nitric acid until all the amido compound had gone into solution. The solution was then filtered, a large quantity of alcohol added, and the whole boiled in a flask provided with a reflux condenser until the nitrogen ceased to be given off. The alcohol was then distilled off on the water-bath and was found to smell strongly of aldehyde. Water was now added to the flask, when a heavy oil separated out, which was allowed to settle for a day or two and then distilled in steam until nothing but water passed over.

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[1] Ann. Chem. (Liebig) **183**, 234.

[2] Ibid. **183**, 234.

The residue.—The non-volatile residue left in the flask consisted of a tarry mass which was filtered off and treated with alcohol. A portion dissolved, coloring the solution deep red, but from the solution no crystals could be obtained by concentrating. The filtrate was neutralised with an alkali and also evaporated to crystallisation, but nothing but the nitrate could be isolated.

The distillate.—The contents of the receiver were allowed to settle and then filtered, the precipitate dried and dissolved in alcohol. This alcoholic solution was then subjected to fractional crystallisation. The melting-point of the different fractions, however, remained constant at about 56° to 58° even to the very last portion. From the agreement of the melting-point and solubility in alcohol and crystalline form, it was concluded we had here to deal with the α-nitro-naphthalene. A small quantity of the substance was reduced with iron and acetic acid, when the well known α-naphthyl-amine was obtained. A determination of the nitrogen in the nitro compound by the modified Kjeldahl method gave the following results:

0.5420 gram gave 0.0535 gram ammonia.

	Calculated for $C_{10}H_7NO_2$.	Found.
N	8.09 per cent.	8.12 per cent.

Again, the only product of the decomposition of the diazo compound in alcohol is the nitro-naphthalene. *The hydrogen reaction alone takes place.*

From 4.8 grams of the α_1-nitro-α_2-naphthyl-amine, 2.53 grams of α-nitro-naphthalene were obtained, which corresponds to a conversion of about 57 per cent. of the diazo compound into α-nitro-naphthalene.

Summary.

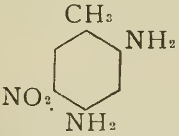
The results of this work may be summed up as follows:

The β_2-nitro-α_2-diazo-naphthalene sulphate, when decomposed in alcohol, gives only β-nitro-naphthalene. The yield of the nitro-naphthalene is very good, corresponding to a conversion of about 84 per cent. of the diazo compound used.

The α_2-nitro-β_2-diazo-naphthalene sulphate gives only α-nitro-naphthalene when decomposed in the same manner with alcohol. The yield here was not so good, corresponding to a conversion of only about 52 per cent. of the diazo compound in this way. The α_1-nitro-α_2-diazo-naphthalene nitrate also gives only α-nitro-naphthalene when decomposed in alcohol. Here, too, the yield was not large, corresponding to a conversion of about 57 per cent. of the diazo compound.

From these results it will be seen that in the case of the diazo compounds obtained from these nitro-naphthyl-amines, the hydrogen reaction alone prevails when these compounds are decomposed in alcohol. Similar results were obtained by Remsen and Graham[1] in the decomposition of the diazo compounds made from the ortho-, meta- and para-nitraniline. In these cases also the hydrogen reaction alone took place. The influence of the nitro group is the same, therefore, both in the benzene and the naphthalene compounds, and the position of the nitro group with reference to the diazo group seems to have no influence on the reaction, the hydrogen reaction taking place in all cases.

It is a matter of interest to note that among all the substituted diazo compounds which give the ethoxy group in place of the diazo group when decomposed by alcohol, only two compounds containing the nitro group have been recorded. One of these is the diazo compound obtained from nitro-toluylene-diamine,[2] $C_6H_2\begin{cases} CH_3(1) \\ NH_2(2) \\ NH_2(4) \\ NO_2(5) \end{cases}$. On treating an alcoholic solution of this substance with nitrogen trioxide and boiling, the ethyl ether of nitro-cresol was obtained having the formula $C_6H_3\begin{cases} CH_3(1) \\ OC_2H_5(2). \\ NO_2(5) \end{cases}$ In other words



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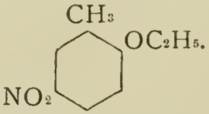

Here one of the diazo groups, ortho to the nitro group, was replaced by hydrogen, plainly showing the influence of the nitro group on the course of the reaction; while the other diazo group, para to the nitro group *but ortho to the methyl group*, was substituted by the ethoxy group. It has already been shown in a previous paper[3] that the methyl group in the *ortho* position brought about the ethoxy reaction alone, and in the para position the hydrogen reaction; and it will be seen that the influence of the ortho methyl group is stronger here even than that of the para-nitro group to induce the hydrogen reaction. It must be noted, however, that the influence both of the nitro group and of the methyl group was in the same direction in the case of the diazo group which was replaced by hydrogen, and in opposite directions in the other case.

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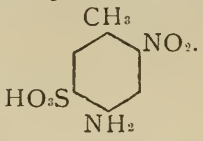
[1] This Journal **11**, 319.

[2] Ber. d. chem. Ges. **7**, 1212; Ann. Chem. (Liebig) **217**, 155.

[3] This Journal **9**, 337.

The other compound is one mentioned by Limprich,[1] and also by von Pechmann.[2] It is nitro-toluidine sulphonic acid, having the structure represented by the formula When the diazo compound obtained from this substance was decomposed by sodium and alcohol it gave the ethoxy compound. When decomposed in a sealed tube with alcohol alone at 100°, however, it gave only nitro-toluene-sulphonic acid, as we would naturally expect, so that it appears that the sodium here exercises some influence, and this case can hardly be cited as an exception to the general rule that the tendency of the nitro group when present in the molecule of a diazo compound, is to induce the hydrogen reaction when the compound is decomposed in alcohol. A very large number of cases might be mentioned in proof of this statement, and only one exception, viz. nitro-toluylene-diamine.



Cornell University, *Nov.* 25, 1891.

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[1] Ber. d. chem. Ges. **18**, 2185.

Ann. Chem. (Liebig) **173**, 215.

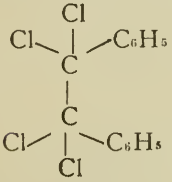
REVIEWS AND REPORTS.

STEREOCHEMISTRY.

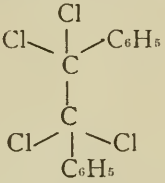
(*Continued from* p. 588, *Vol.* 13.)

Already the general theory of Wislicenus has received the support of quantitative experiments. For example, the formula of tolane tetrachloride has three configurations (*A*, *B*, *C*), in which chlorine atoms occupy "corresponding" positions:

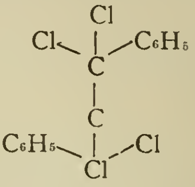
A



B

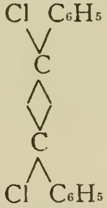


C

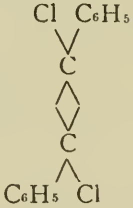


If two atoms of chlorine be removed by a reducing agent, as zinc, the removal will presumably take place only when these chlorine atoms are in corresponding positions; hence only the three configurations given need be taken into account; of these *A* only can yield the unstable dichloride I, while both the other configurations will yield the stable dichloride II:

I.



II.

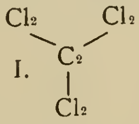


At a temperature high enough to cause incessant relative rotation of the upper and lower halves of all the tetrachloride molecules, there will be then, for every molecule in a position to yield the unstable, two molecules in a position to yield the stable dichloride. Accordingly experiment showed that at 80° C. one-third of the reduction-yield consisted of the unstable and two-thirds of the stable isomer.[1] As the temperature falls the directive affinities regain the upper hand; in centers of heat-disturbance rotation continues and produces the unfavored configuration *A* as before, but in other parts of the mass the favored configurations *B* and *C* occur alone; accordingly, if the reduction is carried out at 20° C. considerably more than two-thirds of the yield consists of the stable dichloride.

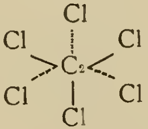
[1] Blank: Ann. Chem. (Liebig) **248**, 27; and comp. This Journal **12**, 231.

These results also throw light on the much-discussed problem as to the circumstances in which relative rotation of singly-linked carbon atoms occurs, and as to the number of isomers resulting. The results show the rotation to depend on the temperature much as dissociation does; and they show the existence of two isomers, the rotating and the non-rotating, of which the former yields on reduction both dichlorides, the latter the stable dichloride only. For some substances the temperature of regular rotation may lie below the ordinary temperature. According to Wislicenus[1] this must be the case when the six radicles attached to the two carbon atoms are all alike; then there will be "free rotation," *i. e.*, rotation practically free from resistance, caused therefore by the slightest heat-disturbance—any temperature above absolute zero. Auwers and Meyer[2] have again brought forward this view and maintain that otherwise there would be two formulæ for a substance like perchlorethane representing two different forms of the substance equally stable:

I.



II.



These formulæ are supposed to be viewed from above; in I the lower chlorine atoms are directly under, in II half way between the others. Since in reality there is only one compound of the formula C_2Cl_6, we must assume, it is said, perpetual relative rotation of the upper and lower chlorine groups. It has been objected[3] that if chlorine be supposed to repel chlorine, the only permissible formula is the second. If, on the other hand, we prefer to assume that chlorine attracts chlorine, only the first configuration will be stable. In either case the necessity for the assumption of free rotation disappears.

Bethmann[4] approached this subject from quite a different side. He determined the affinity-constant of various organic acids by measuring their electric conductivity. In the case of succinic acid, he concluded that no relative rotation of the central carbon atoms takes place "because all the samples of the acid examined gave the same constant." This very fact that all samples of succinic acid have the same properties, *i. e.* that there is only one succinic acid, had been used by Victor Meyer to show that in it rotation is perpetual. In reality the fact proves only that one or other of these views is correct:[5] either no position is of superior stability, or one position is so far superior that no other can compete with it. However, other facts observed by Bethmann are, as will be seen, so easily explained by supposing the relative positions of the radicles composing succinic acid to be permanent in the absence of disturbing influences, that V. Meyer now accepts this view. Baeyer explains some of his results (see *post*) on the same assumption, which is in accord also with the opinions of Van't Hoff and Wislicenus. On the other side stands Bischoff,[1] as we shall see; apparently alone.

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[1] Räumliche Anordnung, p. 14.

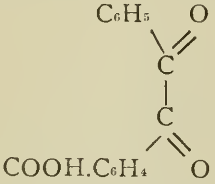
[2] Ber. d. chem. Ges. **23**, 2082. It is here stated that according to Wislicenus the rotation will be free when the six radicles are not alike. But see the passage in the "Räumlicbe Anordnung" just cited.

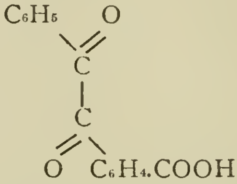
[3] J. prakt. Chem. (2) **43**, 124. Comp. Bischoff: Ber. d. chem. Ges. **24**, 1093.

[4] Ztschr. phys. Chem. **5**, 385.

[5] Comp. Warder: Am. Ass. Adv. Sci. **39**, 111.

Where no one position of the six peripheral radicles is pre-eminently stable, there may, it has been said, be two or more positions of equilibrium; in this case there will be observed among ethane derivatives an isomerism analogous to that at present known only among ethylene derivatives. The two mono-carboxyl ortho-derivatives of benzil may prove to be an instance of such isomerism (Graebe[2]):





In the meantime the simple statement of Van't Hoff stands unshaken: "If the mutual action [of the indirectly connected radicles] depends, as every known force does, on the distance and the nature of the radicles in question, there will be among the possible positions only one which corresponds to the state of stability" (l. c., p. 52).

The Mutual Affinity of Indirectly Connected Radicles—(Baeyer).

Wislicenus had assumed that the greater the difference in the positivity of two radicles in a molecule not directly connected with each other, the greater would be their mutual attraction. Baeyer[3] suggests as a "slight modification" that the attraction corresponds to that which would exist between the two radicles if they were directly connected. Baeyer's objection to the assumption of Wislicenus is based on the properties of the two symmetrical dimethyl-succinic acids, and on the relation between these acids and the two hexa-hydrophthalic acids:

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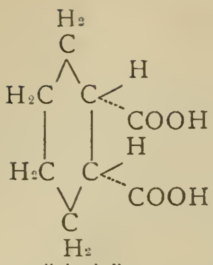
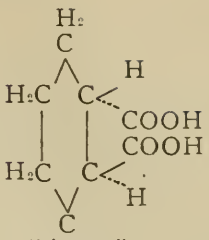
[1] Ber. d. chem. Ges. **23**, 1958.

[2] Ber. d. chem. Ges. **23**, 1344. The suggestion that the benziloximes are a case in point has been withdrawn by its authors (Auwers and Meyer: Ber. d. chem. Ges. **23**, 2402).

[3] Ann. Chem. (Liebig) **258**, 185.

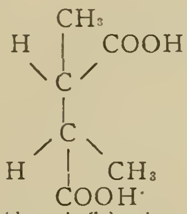


"cis–cis."



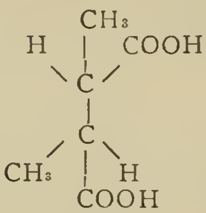
"cis–trans."

The most favored positions for the methyl-succinic acids are, according to Wislicenus,



(theoretically) active.

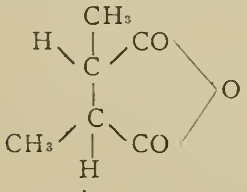
and



inactive.

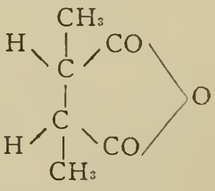
These formulæ do not show why the inactive acid forms an anhydride more readily than the active acid.

Again, the formulæ for the anhydrides would be



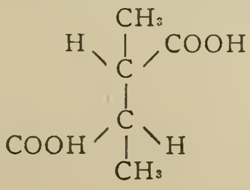
active.

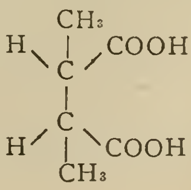
and



inactive.

In the formulæ for the inactive anhydride like groups correspond; according to Wislicenus this anhydride should therefore be the less stable. But the facts point the other way; hence Baeyer argues that correspondence of like groups does not involve instability, and suggests that the favored configurations of the acids have the following formulæ:





In both, methyl is opposite methyl, which explains the similarity in properties between these acids and the hexahydrophthalic acids in which the methylene chain answers to the methyl groups and must evidently have corresponding positions. If we ask why methyl should place itself near to methyl rather than to carboxyl, the answer is that the attraction of methyl for methyl (in ethane) is much greater than that of methyl for carboxyl (in acetic acid).

Thus, in order to explain why fumaric acid is more stable than maleïc acid, we must be prepared to maintain, if we accept Baeyer's hypothesis, that the attraction of H for COOH (in formic acid, two molecules) exceeds the attraction of H for H (in H_2, one molecule) together with the attraction of COOH for COOH (in oxalic acid, one molecule).

The Relative Position of Radicles connected with Two Carbon Atoms singly-linked—(Bethmann).

Having proved that the affinity-constant of a dibasic acid increases as the distance between the carboxyl groups diminishes, Bethmann showed that the introduction of a methyl group increased the constant of succinic acid, and explained this by the formulæ shown in Plate II., which represent how the attraction of methyl for carboxyl draws the carboxyls nearer together, thus raising the constant.

Here it will be seen that the arrangement of Wislicenus for succinic acid is altered. Carboxyl is not immediately over hydrogen, but immediately over a point half-way between the hydrogens which now attract the negative radicle equally.[1] The more strongly positive methyl, however, places itself directly opposite to the carboxyl. Introduction of another methyl group raises the affinity-constant again; that is to say, it causes a further approximation of the carboxyls, or, as Bethmann says, it causes the tetrahedron-axes to incline towards each other.[2]

Bethmann's results are not incompatible with Baeyer's formulæ for the dimethylsuccinic acids, since, as the models show, attraction between the methyl groups might also lead to approximation of the carboxyls.

A comparable case has been investigated in the laboratory of Wislicenus by Reisse, who examined the effect of the successive substitution of chlorine for hydrogen upon the decomposition of the sodium chlorlactates, which, on heating, yield sodium chloride, carbon dioxide and a chloraldehyde; *e. g.*,

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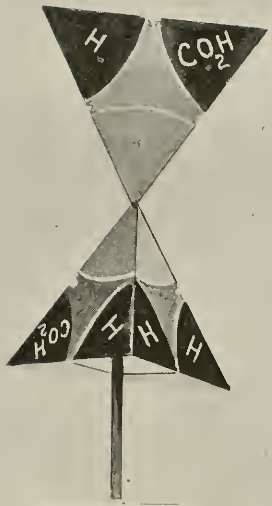
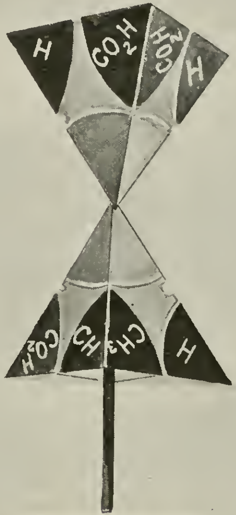
[1] W. P. Evans (Ztschr. phys. Chem. **7**, 337) also finds his results explicable only on the assumption that such "middle positions" represent the favored configuration in molecules analogous in structure to succinic acid.

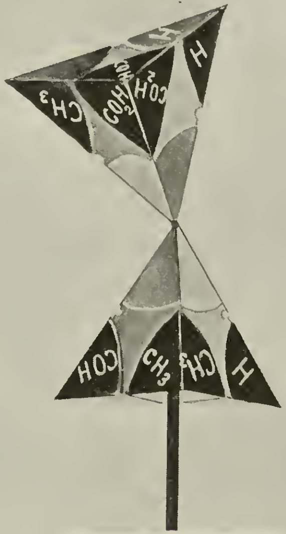
[2] This conception would be necessary if the tetrahedra were regular. The tetrahedra $R - CH.CH_3$ COOH and R′ — CH.H.COOH are, however, irregular (see note p. 4a) and dissimilar; their axes probably already not in a line Moreover, the inclination suggested represents more than is proved, viz., not only diminution of the distance between the carboxyl and probably between the methyl groups, but an increase of the distance between the hydrogen atoms. Still we may accept Bethmann's figures as a rough illustration of the facts.



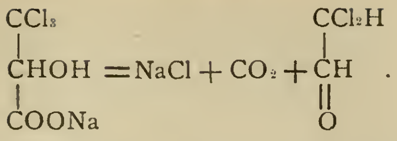
Succinic Acid
(Bethmann).



Methylsuccinic Acid
(Bethmann).



Dimethylsuccinic Acid
(Bethmann).



$$\begin{array}{l}CCl_3\\ |\\ CHOH\\ |\\ COONa\end{array} = NaCl + CO_2 + \begin{array}{l}CCl_2H\\ |\\ CH\\ \|\\ O\end{array}\ .$$

According to Bethmann's theory, the formulæ of the chlorlactates would be

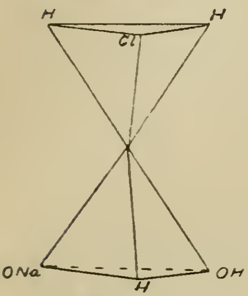


FIG. 25.

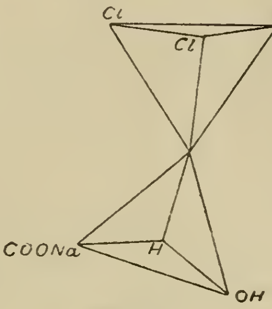


FIG. 26.

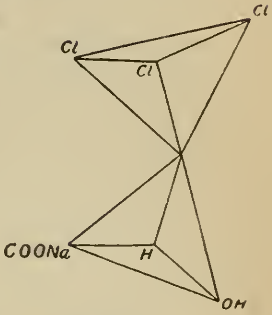
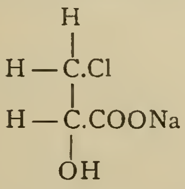


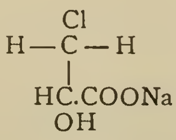
FIG. 27.

In the dichlorlactate the attraction of the two chlorine atoms for the two positive groups opposed to them causes bending and an approximation of these four radicles, but an approximation checked somewhat by the attraction of hydrogen for hydroxyl on the other side of the molecule. The substitution of chlorine for this hydrogen lessens the check, and in the trichlorlactate the approximation of sodium and chlorine is greatest. This should therefore be the readiest to decompose with formation of sodium chloride, and in fact it is so, the dichlorlactate also decomposing more readily than the mono-chlorlactate. Reisse's paper, however, was published a few days before the theory of Bethmann, and Reisse's explanation is different. "The three configurations of the trichlorlactate are all equally qualified to form sodium chloride, while only two configurations of the di- and only one (I) of the monochlorlactate (I, II, III) is capable of this decomposition":



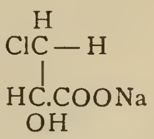
$$\begin{array}{l}\quad\ H\\ \quad\ |\\ H-C.Cl\\ \quad\ |\\ H-C.COONa\\ \quad\ |\\ \quad\ OH\end{array}$$

I.



$$\begin{array}{l}\quad\ Cl\\ H-C-H\\ \quad\ |\\ \ \ HC.COONa\\ \ \ OH\end{array}$$

II.



$$\begin{array}{l}\quad H\\ ClC-H\\ \quad |\\ HC.COONa\\ \ OH\end{array}$$

III.

Bethmann's hypothesis of the approximation of the carboxyl groups in the case of alkyl-succinic acids has been tested in another way. If approximation of the carboxyls really takes place, this should show itself in their readiness to combine with exit of water, *i. e.* the introduction of methyl groups should facilitate the formation of anhydrides. Now Bischoff[1] finds that with regard to the ease with which they form anhydrides the methylsuccinic acids may be arranged in the following series: tetra-, tri-, di-, and mono-methylsuccinic acid. No explanation analogous to that given by Reisse for the decomposition of the chlorlactates is applicable here. Bethmann's hypothesis is; [and if we accept it we must reject the assumption, compatible with Reisse's view but incompatible with that of Bethmann] that the distance between two radicles connected by means of two carbon atoms varies between limits whose ratio is known: the minimum bearing to the maximum distance the ratio of the height of a regular tetrahedron to the length of its edge.

Further determinations of the affinity-constants of substituted succinic acids show, however, that the generalisations of Bethmann do not always hold good and "cut off all possibility of establishing laws generally valid" (Walden[2]). Ethyldimethyl-succinic acid *e. g.* has nearly the same constant as dioxysuccinic acid (mesotartaric acid), or the result of replacing three hydrogens by positive groups is nearly the same as that of replacing two hydrogens by negative groups.

The Space occupied by the Radicles in a Molecule—(Bischoff).

Bischoff, like Bethmann, had inferred that the carboxyl groups approach one another, and added that it may be supposed that the substitution of alkyl groups for hydrogen leaves too little room in the molecule for the hydroxyl groups, and hence the formation of the anhydrides. Many interesting applications of the theory of the crowding out of some atoms by others are given. Thus the following formulæ explain why monosodium carbonate, $NaHCO_3$, is stable while carbonic acid, H_2CO_3, cannot exist.

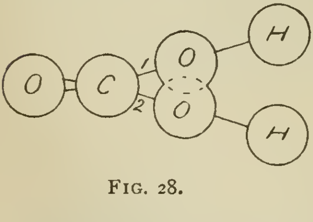


FIG. 28.

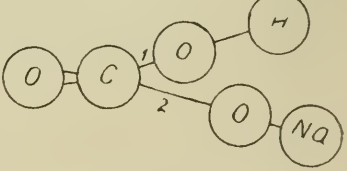


FIG. 29.

The affinity of sodium for oxygen is greater than that of hydrogen. Sodium will therefore bring oxygen nearer to itself and accordingly further from carbon; *i. e.*, the distance (2) in Fig. 29 is greater than the distance (1). Through this arrangement the groups OH and ONa have room to oscillate without collisions. In Fig. 28 the distance 2 is as small as the distance 1 and collisions ensue, which cause splitting off of hydrogen and hydroxyl.

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[1] Ber. d. chem. Ges. 23, 620 and 3419.

[2] Ztschr. phys. Chem. 8, 433.

Further, the substitution of sodium for hydrogen in two hydroxyl groups may alter the angle between these groups.

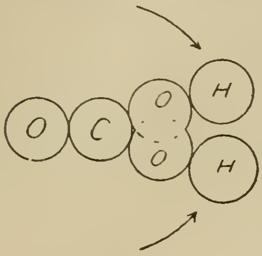


FIG. 30.

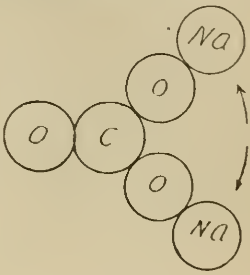
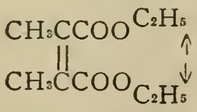


FIG. 31.

Both this and the increased distance of the oxygen atoms from the carbon atom have to be taken into account in considering the probable space-relations of the atoms. If, instead of sodium, alkyl groups be substituted for hydrogen in the hydroxyls, the results are similar and similarly explained. Hence it is that ethyl pyrocinchonate, $\begin{array}{l} CH_3CCOOC_2H_5 \\ \quad\;\| \\ CH_3CCOOC_2H_5 \end{array}$, can exist while the acid is known only as anhydride, $\left.\begin{array}{l} CH_3CCO \\ \quad\;\| \\ CH_3CCO \end{array}\right> O$.

This answers the objection of Anschütz[1] that where there is no room for hydroxyl groups there can *a fortiori* be no room for ethoxyl groups. In fact, ethyl does not occupy the space indicated by the ordinary formulæ $\begin{array}{l} CH_3CCOOC_2H_5 \\ \quad\;\| \\ CH_3CCOOC_2H_5 \end{array}$, (the space which would be occupied by hydrogen $\begin{array}{l} CH_3CCO\,OH \\ \quad\;\| \\ CH_3CCOO\,H \end{array}$); but owing to its more strongly positive nature the ethyl group makes room for itself in a molecule from which the weaker hydrogen atom, though smaller, is excluded:



$$\begin{array}{l} CH_3CCOO^{C_2H_5} \\ \quad\;\| \qquad\qquad\quad \updownarrow \\ CH_3CCOO_{C_2H_5} \end{array}$$

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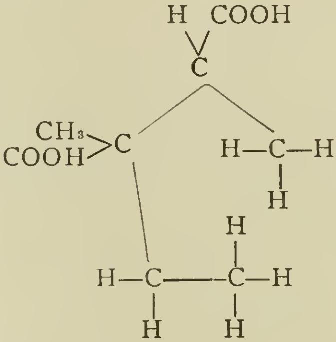
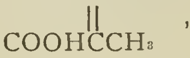
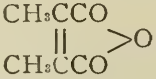
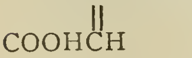
[1] Ann. Chem. (Liebig) **259**, 145.

The idea of the crowding and collision of the groups in a molecule led Bischoff to a new conception, to his theory of "dynamical isomerism."

The Relative Motion of Indirectly Connected Radicals—(Bischoff).

If lack of space for the carboxyl groups of an acid cause exit of water, is this not because the hydroxyl groups come into collision, because the atoms of each come within the range of action of the atoms of the other? This leads to the question: What then will happen if the alkyl groups of the acid come into collision? Five carbon atoms singly-linked form almost a complete ring (see p. 574 *ante*); hence collisions may well occur between the radicles forming the ends of such a chain; *e. g.* between the alkyl groups of ethyl-dimethyl-succinic acid:



That the alkyl groups would be driven from the molecule was not probable; but further rotation might be hindered and each driven back along the path by which it came. The models show that this would lead to new cases of isomerism. Bischoff, however, could find no isomers not accounted for by Van't Hoff's theory, but was led to develop his own theory in order to explain the properties of the isomers he did find. He agrees with Baeyer that methyl does not repel methyl (I); and with Wislicenus that carboxyl repels carboxyl (II); further, he maintains that carboxyl repels methyl (III), urging as proof the non-existence of dimethyl-fumaric acid,  $\begin{array}{c}CH_3CCOOH\\ \|\\ COOHCCH_3\end{array}$, and the impossibility of forming it from pyrocinchonic acid,  $\left.\begin{array}{c}CH_3CCO\\ \|\\ CH_3CCO\end{array}\right>O$; one methyl and one carboxyl group may, however, exist together (mesaconic acid  $\begin{array}{c}CH_3CCOOH\\ \|\\ COOHCH\end{array}$). It follows: *a*, that under the repellent action of methyl groups a carboxyl may be forced to approach another carboxyl (see formulæ for tri- and tetramethyl-succinic acids); hence, (*α*) ready formation of anhydride; (*β*) rise of conductivity.

b. There is only one asymmetrical dimethyl-succinic acid, that in which carboxyl is removed from the methyl groups.

c. Ordinarily, carboxyl groups separate freely; succinic anhydride forms the acid with cold water:

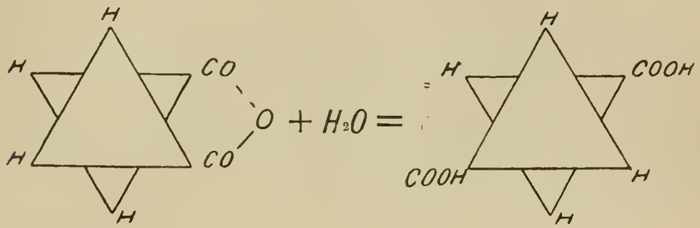


FIG. 32. FIG. 33.

But, when separation of the carboxyl groups would cause them to approach methyl, force must be used to effect it—heating with water under pressure.

As to III and *a* it may be said that mono- and dimethyl-succinic acids conduct better than succinic acid itself. Bischoff's formulæ (see figures) do not explain this; whereas Bethmann, assuming that methyl *attracts* carboxyl, was able to do so. If we express now Bischoff's conclusions in the phraseology of his theory, the result is not more convincing. He attributes, "with Van't Hoff," free rotation (see *ante*, p. 59) to ethane and its mono-derivatives, but supposes the position of rest for ethane to be

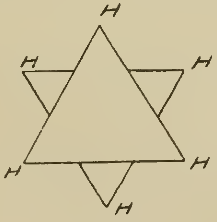


FIG. 34.

Van't Hoft has, however, long since given up (if he ever held[1]) the hypothesis of free rotation (*ante*, p. 60); and *free* rotation (*i. e.* rotation free from all resistance) is incompatible with rest at any temperature above absolute zero.

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[1] Several authors say he did; Auwers, "Entwicklung," p. 8; Warder, *l. c.* Marsh encourages a similar view, "Chemistry in Space," p. 124. But the passage in "La chimie dans l'espace," p. 8, amounts only to saying that *if* rotation takes place, the different phases passed through do not represent different isomers.

"In other ethane-derivatives free rotation of the systems round the common axis is limited, and assuming collision of carboxyl with carboxyl and with alkyl groups, we may indicate by the dotted lines the path through which one of the carboxyl groups will oscillate." (See figures.) Here collision seems to be but another word for repulsion. The figures represent the favored configurations, "those in which the constituents least hinder one another's oscillations."

Here the formula for monomethyl-succinic acid which indicates collision between carboxyl and methyl, is in contradiction with Bischoff's statement (*l. c.* p. 1089) that the neighborhood of one methyl to one carboxyl group causes no collision. At present, however, the theories of Bischoff are apparently in a transition stage, and it is enough here to have indicated the new possibilities which they open up for stereochemistry.

Conclusion.

We know by experiment that (1) crystalline compounds $C(R_1)_4$ belong to the regular system; (2) Compounds $CR_1R_2R_3R_4$ are optically active in solution; and (3) present a peculiar isomerism; (4) In substances $C(R_1)_2R_2R_3$ these peculiarities are lacking; (5) Substances $C_2R_1R_2R_3R_4$ are not optically active; but (6) present an isomerism different from that referred to in (3); Further, that (7) carbon rings are specially stable when they consist of five or six atoms; (8) Five carbon atoms form a ring of distinguished stability when combined with ten hydrogen atoms or their equivalent; (9) Six carbon atoms form such a ring with six hydrogen atoms or their equivalent.

Most of these statements of fact hold good for a considerable number of compounds; but, theory aside, each stands alone disconnected from all the others. Now all these general facts are connected together by the theories of Van't Hoff, and the first six of them by the theories of Le Bel.[1] Van't Hoft's theories being the more detailed require confirmation in detail. It is this confirmation which has in so many instances been brought by the investigation of particular cases of isomerism, although it has been seen also that in many cases more facts are needed before the connection between those already known can become apparent.

Our knowledge of the interaction of the radicles connected with carbon is in its first stage. Wislicenus assumed that this knowledge sufficed to enable us to represent with sufficient accuracy the configuration of ethane derivatives such as the dimethylsuccinic acids. Yet for these acids Baeyer, Bethmann and Bischoff have all suggested configurations differing from that of Wislicenus as well as from one another, so that there is now in the field almost as great a variety of these configurations as is compatible with the

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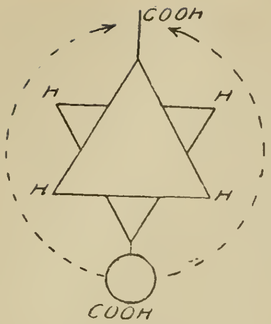
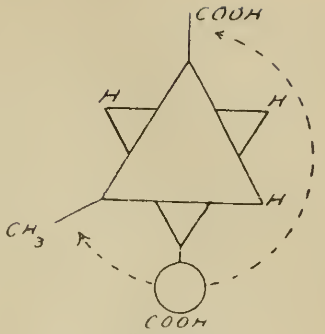
[1] The connection between (5) and (6) depends on the proof that in ethylene derivatives the radicles connected with carbon are in one plane, for which see Le Bel, Bull. Soc. Chim. **37**, 300.



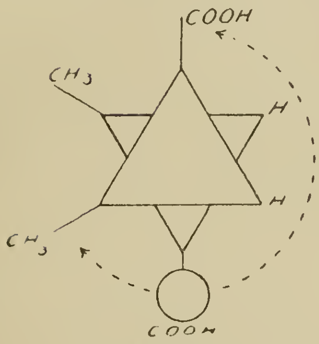
Succinnic.

FIG. 35.



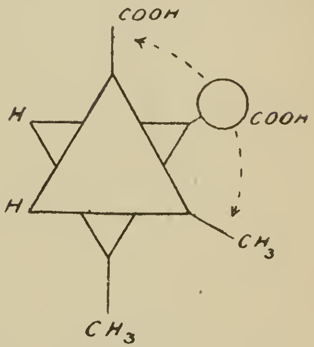
Monomethyl

FIG. 36.



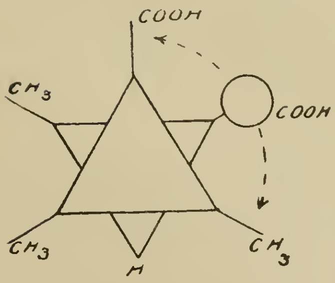
Para-dimethyl-

FIG. 37.



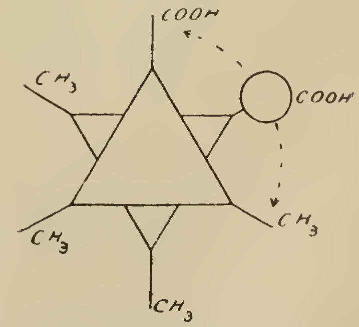
Anti-dimethyl-

FIG. 38.



Trimethyl-

FIG. 39.



Tetra-methyl-succinic acid.

FIG. 40.

theory of Van't Hoff (*ante*, p. 60) concerning ethane derivatives; yet not one configuration incompatible with it.[1] Thus that theory which at first startled chemists by the boldness with which it attempted so closely to define the positions of atoms, is now seen to be no less remarkable for the caution with which it avoided a definition closer than the facts warranted; advancing its conclusions at once up to the limits of just inference, the theory never pushed speculation beyond these limits. And recent stereochemical investigation may be described as an attempt to extend the limits within which Van't Hoff was confined, by determining the details of the interaction of indirectly connected radicles, especially in ethane derivatives, with a view to fixing the relative position of these radicles; this action may depend on a number of quantities, as (1) the affinity of the radicles for one another, (2) their affinity for carbon, (3) the distance between their centers of gravity, (4) the space occupied by them, (5) their relative motion. For no pair of radicles is any one of these quantities known absolutely, nor can we compare approximately one pair of radicles with another pair with respect to any one of these; usually we cannot say for which pair the quantity would be greater, and the uncertainty will continue as long as doubt remains concerning Wislicenus' "positive negative" hypothesis, or the proper substitute for it. These considerations render evident at once the extent and the importance of the work yet to be done; if stereochemistry is to advance, the problems indicated must advance side by side towards solution. And the continual attention which is now devoted to stereochemistry by German chemists, the fact that a stereochemical solution of each new structural mystery is ever held in mind, and the mass of work upon this subject constantly pouring from the laboratories of such investigators as Wislicenus, Baeyer and Bischoff, justify our confidence that the questions at present in dispute are on the way to settlement. Among the new problems then to be attacked will be the space-relations of elements other than carbon. Already the stereochemistry of nitrogen has formed the subject of many investigations, and this will be considered in a later review.

ARNOLD EILOART.

THE CHEMICAL ANALYSIS OF IRON. A Complete Account of all the best known methods for the Analysis of Iron, Steel, Pig Iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR. Second Edition. Philadelphia: J. B. Lippincott & Co., 1891.

When Mr. Blair's book on the Chemical Analysis of Iron first appeared, chemists immediately recognised that they had acquired a valuable and almost unique contribution to a special branch of analytical chemistry. Nothing had hitherto been written on this subject which approached Mr. Blair's book in completeness, accuracy, and usefulness. In the second edition, which has been called for by the prompt exhaustion of the first, Mr. Blair has still further increased the value of the work by careful revision and by the addition of much new matter. Many of the new processes described have been obtained from chemists of long experience in the laboratories of iron and steel works and represent the results of patient chemical experiment, and of much mechanical ingenuity, in perfecting methods for the rapid analysis of iron and steel—processes red-hot from the works, we might almost say. Mr. Blair mentions briefly—much too briefly, we think—the work of the American members of the International Steel Standard Committee, whereby our established practice and cherished theories regarding the determination of carbon in steel have been badly disturbed. This section of the book—the determination of carbon—is, from the standpoint of historical completeness, all that could be desired. But it still lacks the critical element which we think it needs. It will be found bewildering by the beginner who consults it to learn which are the most recent or most generally used processes. Mr. Blair has uniformly avoided a personal expression of opinion as to the accuracy of the processes he described with praiseworthy minuteness. There may be a wise prudence on his part in this restraint, but his readers would be often glad to know to which of the processes he gives the preference in his own practice. Book-makers are so often merely compilers that we do not ordinarily expect criticism and description to go hand-in-hand. But Mr. Blair could unite these processes with sure hand.

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[1] Even Bischoff's oscillation-configurations are not excluded, for we may derive them just as well from the heat-disturbance admitted by Van't Hoff as from the free rotation assumed by Bischoff.

The tables of atomic weights and factors have been thoroughly revised for this edition, and the pages have been provided with a running title which greatly facilitates reference. We could have wished the author had in this edition rejected the use of symbols as abbreviations. If he were consistent in his practice in this regard, we might think he had entered on a crusade against the waste of time and space involved in writing chemical names in full. But when we see in five lines (to take an example at random) "Carbonate of Sodium," "Fe_2O_3," "H_2SO_4," "Titanate of Sodium," and "TiO_2," it looks as if the author were indifferent to the appearance of his (otherwise) handsome pages, and to the established usage of chemical writers. Shortcomings of this kind are the more to be regretted in a book which is largely used by "practical" chemists, who in their rush of work are only too apt to fall into careless forms of expression and writing.

We would like to repeat what was said in a notice of the first edition of the work, and which continued use of the book has fully justified, namely, that teachers of chemistry find this book of great value and convenience. It is impossible for a student to go astray in his work when he has this book in his hand.

THOMAS M. DROWN.

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY. By SAMUEL P. SADTLER, Professor of Organic and Industrial Chemistry in the University of Pennsylvania. 8vo. J. P. Lippincott & Co., Philadelphia, 1891.

Professor Sadtler's book covers a field never before completely reviewed in any single work in English. The subjects treated are the following: petroleum, fats and oils, essential oils, sugar, starch, fermentation industries, milk industries, vegetable and animal textile fibres and their utilisation, leather, glue and gelatine, destructive distillation of wood and coal, artificial coloring matters, natural dye-colors, bleaching, dying and textile printing. Each subject is subdivided into five sections, viz.: materials, processes, products, analytical tests and methods, bibliography and statistics. With so wide a field to cover in a single volume of 500 pages, the treatment of each subject is necessarily brief, and many details which would have added to the interest of the work are unavoidably omitted. On the whole the book is a remarkable example of successful and satisfactory condensation, a result largely due to very systematic arrangement of the material.

A great deal of patient labor has been expended by the author in collecting statistics in regard to the various industries. These are of value in estimating the relative importance of different localities of production, and will prove a great convenience to teachers of industrial chemistry. The figures are well brought up to date, for the most part including the year 1890. The lists of books of reference are also full and valuable. Except in the case of analytical methods, references to periodical literature are not generally given. This is to be regretted, as many articles of great interest on the subjects treated have lately appeared, such as the papers on petroleum by Mendelejeff and Redwood in the Journal of the Society of Chemical Industry.

An excellent feature of the book is the full account given of American processes of manufacture. In this respect the work contains much that is not to be found elsewhere. Fuller information in regard to the particular sections of the country where the important industries are chiefly developed would have given increased interest to the processes described. A number of ingenious graphic outlines of the chief industries are given; these are very instructive, and excellent for purposes of review. Care has been taken to give credit to the authors in case of tables or illustrations taken from other works. The chief criticism which the reader will be disposed to make will be on the ground of too great brevity, for in examining so good a book it is impossible to resist the regret that there is not more of it. The chapter on artificial coloring matters is a very satisfactory brief outline of this complicated subject, and presents the most important facts in regard to the coal-tar colors in a way which will be welcome to English-reading students. The book closes with an appendix containing useful metric, thermometric and specific gravity tables.

S. B. N.

A SYSTEM OF INORGANIC CHEMISTRY. By WILLIAM RAMSAY, PH. D., F. R. S., Professor of Chemistry in University College, London. London: J. & A. Churchill, 1891. xvi + 700 pp. 8vo.

The author has attempted in this book to bring into the subject of inorganic chemistry the same order that is characteristic of organic chemistry. He finds in the periodic law the basis of a rational classification of the elements and their compounds. On this subject he remarks: "Nearly twenty-five years have elapsed since the discovery by Newlands, Mendeléeff, and Meyer of the periodic arrangement of the elements; and, in spite of the obvious guide to a similar classification which it furnishes, no systematic text-book has been written in English with the periodic arrangement of the elements as a basis." Before proceeding farther it may not be out of place to point out that this statement needs modification. Richter's Inorganic Chemistry, of which we have an English translation, and the "Text-book of Inorganic Chemistry" by the writer of this notice, are both based upon the periodic law. To be sure, in neither one is the periodic arrangement followed pedantically; though, on the other hand, the deviations from the paths pointed out by the law are few—not greater in number in fact than those of which Professor Ramsay himself has been guilty, if to deviate at all be a crime. As to this he says: "The periodic arrangement has been departed from in two instances: the elements chromium, iron, manganese, cobalt, and nickel have been taken after those of the aluminium group; and the elements copper, silver, gold, and mercury have been grouped together and considered after the other elements. It appeared to me that the analogies of these elements would have been obscured, had the periodic arrangement been strictly adhered to." While arresting attention to an error of statement on the part of our author, it appears that the writer of this heartily agrees with him that the periodic law is the best foundation at present known for a rational treatment of the science of chemistry.

Among the reasons which, according to Professor Ramsay, have led to the prevailing unsatisfactory treatment of inorganic chemistry are:

1. "That the ancient and arbitrary line of demarcation between the non-metals and the metals has been adhered to;"

2. "That too great importance (from the standpoint of pure chemistry) has been assigned to the distinction between acid hydroxides and basic hydroxides (acids and bases), which has tended to obscure the fact that they belong essentially to the same class of compounds, viz., the hydroxides;" and

3. "That the chemistry of text-books has almost always been influenced by commercial considerations."

As regards the first two reasons it should be remarked that, while no doubt the author is right, on the other hand it is possible to err in the opposite direction, and not lay enough stress on the differences between the elements, and between their hydroxides, oxides, etc. It is certainly true that a sharp line cannot be drawn between the two classes of elements and between the two classes of hydroxides, etc., but it is also true that there are fundamental differences of some kind between these two classes, and that these differences are among the most important facts in the field of chemistry, and any system that does not emphasize them is not true to nature. The pointing out of analogies is not the only thing necessary; differences must also be pointed out. A satisfactory picture of the field can be given only by taking account of the lights and shadows. A map serves a very useful purpose, but it fails to give us much information of the highest value as regards the character of the country represented. An examination of the book under consideration shows that much has been sacrificed to systematic arrangement.

As regards the third reason above given, viz., the influence of commercial considerations, the writer fully agrees with Professor Ramsay. Descriptions of manufacturing processes still play too prominent a part in text-books of chemical science, and students unquestionably get wrong impressions concerning the relations of these processes to the science. It is a step in the right direction to relegate these descriptions to an appendix. By the above it should not be understood that there is any objection to teaching the students something about the manufacturing processes. On the contrary, it is well to call their attention to important applications of chemical truths. But such treatment as will serve unduly to magnify the importance of these processes or to create the too common impression that the chief object of the science is to furnish such methods, is to be avoided.

Having thus briefly considered the method of the book let us turn to the execution. Here there can be no hesitation in saying that the author has most conscientiously carried out the plan adopted by him, and he has therefore produced a book of value, though, like all other books, it has its limitations. First as to the plan. The subject is divided into nine parts. Part I treats of matters introductory and historical; Part II of the elements, arranged in six groups; Part III of the halides; Part IV of the oxides, sulphides, selenides and tellurides; Part V of the borides, carbides and silicides; Part VI of the nitrides, phosphides, arsenides, antimonides; Part VII of alloys and hydrides; Part VIII of spectrum analysis, the atomic and molecular weights of elements, and the molecular weights of compounds, the periodic arrangement of the elements; Part IX of processes of manufacture, commercial preparation of the elements, utilisation of sulphur dioxide.

This plan is well adapted to a work of reference, and it may be predicted that whatever success the book may meet with will be due to the fact that it contains brief and accurate descriptions of a large number of substances arranged in an orderly way. In this respect it is superior to any existing book of its size. Many compounds that find no place except in the large dictionaries or the largest text-books are here mentioned and assigned their proper place in the system. While helping the student to get information in regard to individual compounds, long continued use of a book of this kind for reference would serve to impress upon his mind the general relationships between the compounds. For such use the book can be cordially recommended.

But from what has been said it will be concluded that the book does not appear to be as well adapted to the uses of the student who is trying to inform himself regarding the fundamental principles of chemistry. From a pedagogic point of view the treatment of all the elements at the beginning cannot be commended. The reactions made use of in the preparation of these elements are quite unintelligible to the beginner, and the plan necessitates the introduction of too much that is unintelligible before a single chemical reaction is discussed so fully as to give the student a clear impression regarding it.

Again, the author is unusually conservative in the matter of the conceptions that enter so largely into what is called modern chemistry. The views regarding the constitution of the compounds of carbon held by most chemists make the orderly treatment of organic chemistry possible. The phenomena of substitution and valency, as is well known, are at the basis of the prevailing views. To some it seems that in dealing with inorganic compounds we shall probably be obliged to follow the paths already followed by those who have developed the subject of organic chemistry. Careful study of the phenomena of substitution and valency has, it can be fairly claimed, been of great service in the study of the relations between inorganic compounds. Yet to these phenomena Professor Ramsay gives very little attention. When the subject of valency is first referred to, he says: "For these reasons it is concluded that the general formula of the halides of this group (calcium group) of elements is MX_2, where M stands for metal and X for halogen; that of the members of the lithium group is MX. Lithium and its congeners are termed *monad* or *monovalent* elements in these compounds; beryllium, magnesium and elements of their groups are termed *dyad* or *divalent* in their compounds. But it has been amply shown that *valency*, as the property of acting as a monad, a dyad, a triad element is termed, is not a constant quality of any element: nor in such compounds as KI_3, or in the double halides mentioned, can we tell how the atoms are held together, whether the metal attracts halogen, or halogen attracts halogen, or both attracts both. We are at present without any satisfactory theory to account for such compounds, and must, in the meantime, simply accept the fact of their existence."

Attaching as little importance to the phenomena of valency as the author does, he cannot attach much more to the subject of chemical constitution in the usual sense, and it is therefore not surprising that in general he takes but little advantage of prevailing views on constitution for the purpose of bringing out analogies. Though it is surprising that in some cases of complicated compounds concerning the constitution of which we have practically no knowledge based upon experimental study, as, for example, sphene (p. 313) and the analogous compounds, ultramarine, sodalite, nosean (p. 316)—that in such cases he should give constitutional formulas with some degree of confidence. Again, it is not surprising that the author makes free use of the conception of "double compounds." In this class, indeed, he prefers to put the hydroxides and the hydrosulphides. It may be that, as far as our knowledge of calcium hydroxide as an individual is concerned, the formula $CaO.H_2O$ is as good as $Ca(OH)_2$, but surely convictions reached by the study of chemical compounds in general are worth something. The hydroxide theory has been weighed these last thirty years and it has not been found wanting. That which we regard as evidence of the constitution of the alcohols is also evidence that the metallic hydroxides have the same constitution. To accept the hydroxide view is to simplify the study of a large number of the most important chemical reactions. What has been said concerning the hydroxides is applicable to other classes of compounds. Professor Ramsay would have improved his book by taking fuller advantage of the prevailing conceptions concerning the constitution of chemical compounds.

While the book seems open to some adverse criticism, it is only fair to say that it has many valuable features to recommend it, and especially those students who have got over the first difficulties in the study of chemistry will find it helpful. I. R.

NOTES.

Free Hydroxylamine.

The attempts of Lossen[1] to obtain hydroxylamine in the free state seem to have met with little success. His endeavor to separate the base by distillation after having decomposed the hydrochlorate by means of a strong alkali solution, generally resulted in its decomposition with evolution of ammonia. Victor Meyer, having recently questioned[1] the accuracy of the usual statements with regard to the great instability of free hydroxylamine, C. A. Lobry de Bruyn has now published a preliminary paper,[2] giving the results of his researches in this field up to the present time.

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[1] Ztschr. Chem. [2] **1**, 151; Ann. Chem. (Liebig) Suppl. **6**, 220; **160**, 242.

Since the introduction of the amido group in the place of hydrogen generally results in the formation of a compound with higher melting- and boiling-point than the original compound possesses, it would seem probable, this author thinks, that a compound which bears to water the relation of an amido derivative would be a solid at ordinary temperatures. This reasoning is justified by the facts discovered.

Believing that the presence of water had been fatal to the success of Lossen's experiments, Lobry de Bruyn has employed absolute methyl alcohol as solvent, having found that the hydrochlorate is more soluble in this reagent than in its homologue, absolute ethyl alcohol. In this medium the salt was treated with sodium methylate, after which the mixture was freed by filtration from the sodium chloride formed. The liquid was now found to contain free hydroxylamine, and on exposure to the air gave evidence of but slight decomposition.

On distilling the mixture it was found that some hydroxylamine passed over with the alcohol, but that the amount of loss from this source was lessened by decreasing the pressure inside the distilling apparatus. Finally, under a pressure of but 60 mm., nearly all the alcohol was removed and, by fractioning the residue, a product was obtained which solidified in the receiver, and which, after being several times pressed between layers of filter-paper and dried, was found to consist of hydroxylamine 99.4 per cent. pure. Still purer specimens have since been obtained.

Pure hydroxylamine is a white, odorless solid, crystallising in needles which melt at 33°. Heated rapidly it explodes, the flame produced being of an intense yellow color. It is only slightly soluble in chloroform, benzene, ether, ethyl acetate or carbon bisulphide. It is readily soluble in water, being in fact so deliquescent that the crystals rapidly become liquid when exposed to the air; in this condition it slowly evaporates. Strong aqueous solutions of hydroxylamine, when free from salts and protected from the air, are permanent; a solution containing 60 per cent. of the base was found to be unchanged after having stood for several months. Dilute solutions suffer slow decomposition when boiled.

When protected from the action of alkalies hydroxylamine is stable: care has to be taken, however, that the glass vessels used for its preparation and preservation shall not bring about decomposition, so sensitive is it to the action of even minute quantities of alkali.

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[1] Ann. Chem. (Liebig) **264**, 126.

[2] Recueil trav. chim. **10**, 100.

Bromine and iodine attack the base vigorously, giving rise to the formation of nitrous oxide—

$$2NH_2OH + 4Br = N_2O + 4HBr + H_2O.$$

The difference in the behavior of ammonia and of hydroxylamine towards the halogens is worthy of notice.

A peculiar property of hydroxylamine when in the liquid state is its power to dissolve salts as, for example, sodium chloride; on evaporation the salt is thrown down in crystalline form. Further work in this field is now being prosecuted.

Since the publication of Lobry de Bruyn's paper a short article has appeared,[1] in which the experiments of L. Crismer in the same direction are described. On heating the compound of zinc chloride and hydroxylamine, $ZnCl_2.(NH_2.OH)_2$,[2] Crismer found that the base distilled off and could be condensed in a proper receiver. As, however, the presence of free chloride of zinc is disadvantageous, the two following methods were devised to meet this difficulty:

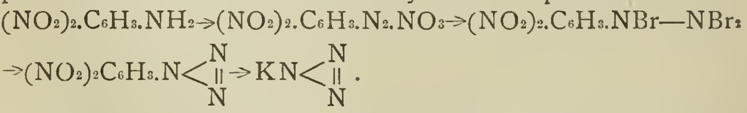
(*a*) The salt was decomposed by heating with anhydrous aniline under a pressure of but 20 mm., a compound of zinc chloride and aniline being produced. The hydroxylamine was condensed in the form of crystals.

(*b*) The salt was placed in a flask with absolute ether and decomposed by a current of perfectly dry ammonia. The free hydroxylamine goes into solution in the ether; distillation in a vacuum serves to remove the ether and to leave the base in a pure condition.

W. W. R.

The Preparation of Hydrazoic Acid.

E. Noelting and E. Grandmougin[3] have devised for the preparation of hydrazoic acid a method which does away with much of the difficulty inseparable from that of Curtius. Noting the fact that the introduction of nitro groups to replace hydrogen atoms in chlor-benzene renders that compound much more sensitive to the action of reagents, these investigators made use of dinitro-aniline, instead of aniline, as a starting-point in their work. Converting this into the corresponding diazo-compound, this into the perbromide, and then decomposing the latter by means of ammonia, they obtained dinitro-phenyl hydrazoate. By the action of alcoholic potash the ether is decomposed with the formation of the potassium salts of hydrazoic acid and of dinitro-phenol. The products of the several reactions may be thus represented:



$$(NO_2)_2.C_6H_3.NH_2 \rightarrow (NO_2)_2.C_6H_3.N_2.NO_3 \rightarrow (NO_2)_2.C_6H_3.NBr{-}NBr_2$$
$$\rightarrow (NO_2)_2C_6H_3.N{<}\begin{matrix}N\\ \|\\ N\end{matrix} \rightarrow KN{<}\begin{matrix}N\\ \|\\ N\end{matrix}.$$

The mixture of the solutions of the salts is acidified and heated, when hydrazoic acid distils off. The investigation will be continued in order to study the behavior of other di-substitution-products of aniline under similar conditions. W. W. R.

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[1] Bull. Soc. chim. (Paris), [3] **6**, 793.

[2] Ibid. [3] **3**, 115.

[3] Ber. d. chem. Ges. **24**, 2546.

The Vapor-density of Ammonium Chloride.

The literature of abnormal vapor-densities has received another addition in a paper by O. Neuberg,[1] who, by the use of an apparatus devised by Lunge and himself, has been enabled to determine the vapor-density of ammonium chloride under greatly diminished pressure.

The apparatus used[2] is a modification of that of Victor Meyer, the novelty consisting in the use of Lunge's "Volumeter" for the collection and measurement of the air displaced from the vaporising-tube through the volatilisation of the substance experimented with. The graduated tube in which the air is to be measured is connected with a reservoir of mercury, as is also a closed tube containing as much air as at 0° and 760 mm. pressure will occupy a volume of exactly 100 cc. when the level of the mercury in it is at the zero-mark. The two latter are so arranged that they can be raised or lowered as the experimenter may desire. By means of a three-way cock the air-measurement tube can be at will connected with the vaporising-apparatus, or, on the other hand, with the outside air.

By successively lowering the reservoir when the vaporising-tube and the measuring-tube are in communication, and raising it again when the latter is open to the air and communication with the vaporising-tube has been cut off, the pressure of air in the apparatus can, if it be desired, be reduced to as little as 20 mm.

The pressure having been reduced to the proper point, and connection between the vaporising-tube and the measuring-tube having been established, the volatilisation of the substance is brought about, the tension being constantly maintained by lowering the reservoir as the level of the mercury in the measuring-tube falls. After equilibrium has been reached, communication with the vaporising-tube is cut off, and the 100-cc. tube and the reservoir are raised until the level of the mercury in all three vessels is the same. Under the conditions the gas in the 100-cc. tube will occupy more than 100 cc. The amount of this expansion being noted, the volume of the air in the measuring-tube is read, and, being expanded in exactly the same proportion as the gas in the 100-cc. tube, its volume at 0° and 760 mm. pressure may readily be deduced. The vaporising-tube can of course be filled with ammonia, hydrochloric acid gas, nitrogen, carbon dioxide, etc., instead of air, if it be so desired.

Using a pressure of 25 mm., Neuberg found the vapor-density of ammonium chloride in a tube filled with air to be (*a*) 1.13 and (*b*) 1.2; at a pressure of 46 mm. and in hydrochloric acid gas, (*c*) 1.5; and under a pressure of 60 mm. and in an atmosphere of ammonia, (*d*) 1.68 and (*e*) 1.71. The theoretical vapor-density of the salt is 1.85, and that of a mixture of the gases ammonia and hydrochloric acid, of course, 0.925.

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[1] Ber. d. chem. Ges. **24**, 2543.

[2] Ibid. **24**, 729.

For sulphur vapor a density corresponding to the formula S_8 was obtained. W. W. R.

Iron-carbon-oxide.

Under the above title, Mond and Quincke—following up the discovery, by themselves and Langer, of nickel tetracarbonyl[1]—announced some months ago[2] the preparation of what they supposed to be the corresponding compound of iron. Ferrous oxalate, reduced in a current of hydrogen at 400°, was subjected to the action of carbon monoxide at a temperature of 80°; under these conditions an exceedingly small quantity of a volatile compound of iron and carbon monoxide was formed, and this on analysis gave figures corresponding to the formula $Fe(CO)_4$. In a recent paper[3] Mond and Langer report later and more successful efforts to obtain the compound in quantity and in pure condition. The details of the method of preparation cannot be given here.

Iron carbonyl is a liquid of sp. gr. 1.466, capable of distillation at the atmospheric pressure. It boils at 102.8 and solidifies below —21°. It is soluble in alcohol, ether, chloroform, and mineral oils. The vapor is decomposed at a temperature of 180° into iron and carbon monoxide. Analyses of the liquid and determinations of the density of its vapor both point to the formula $Fe(CO)_5$ as representing the composition of the substance. The authors therefore propose the name "ferro-pentacarbonyl" for the compound, and are of the opinion that the analyses recorded in the former paper were made with an impure material.

Ferro-pentacarbonyl is not affected by dilute acids at ordinary temperatures; concentrated nitric acid, chlorine-water and bromine-water, however, convert it into the corresponding ferric compounds. Alcoholic solutions of the alkalies dissolve ferro-pentacarbonyl without escape of gas. With mercuric chloride a compound is produced containing mercury, iron, chlorine and carbon monoxide; analyses did not, however, give figures from which a definite formula could be deduced.

When exposed to the light, ferro-pentacarbonyl decomposes with the evolution of carbon monoxide and the formation of yellow, tabular crystals resembling flakes of gold. Analyses of these seem to indicate a composition to be represented by the formula $Fe_2(CO)_7$. It should be said that the authors were unable to make molecular-weight determinations by either the vapor-density or the freezing-point method. The behavior of re-agents toward this latter compound is for the most part the same as towards ferro-pentacarbonyl. W. W. R.

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[1] J. Chem. Soc. **57**, 749; Abstract, This Journal **13**, 70.

[2] J. Chem. Soc. **59**, 604.

[3] Ibid. **59**, 1090.

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RESEARCHES ON THE DOUBLE HALIDES.

By Ira Remsen.

In an article[1] published about two years ago I reviewed the evidence as to the nature and structure of the double halides. Attention was called:

(1) To the large number of the substances known as double halides.

(2) To the simplicity of the law governing the composition of these compounds.

(3) To the analogy of these compounds to the oxy-salts.

(4) To the arguments that lead to the conclusion that there are in general two classes of halides, which are to be regarded as basic and acidic, and which bear to each other relations like those that basic oxides bear to acidic oxides.

(5) To the arguments which appear to me fully to justify the conclusion that in the double halides we have a double halogen atom playing the same rôle that the linking oxygen plays in oxy-salts.

I have reason to believe that the views expressed in the article referred to have met with the approval of many. On the other hand, I am aware that there are some who are not willing to accept these views. The only arguments, however, that, so far as I know, have been put forward in opposition, are those contained in Professor Ramsay's recent book "A System of Inorganic Chemistry,"[1] and a brief comment[2] by W. Ostwald in connection with an abstract of my article. The latter deserves mention in this place for the reason that the writer of the abstract has evidently overlooked an essential statement of my article. He calls attention to the fact that potassium ferrocyanide, $K_4Fe(CN)_6$, or $Fe(CN)_2.4KCN$, is an exception to the law of composition of the double halides pointed out by me. To this it need only be remarked that nitrogen compounds, at least the double halides containing ammonium, were distinctly excepted by me. On this point I here quote my own words: "The examples given in the above tables are fair representatives of the whole class of double halides, except that all ammonium compounds are omitted. The double halides formed with halogen salts of ammonium are very numerous, and many of them are quite complicated. There are indeed ammonium salts known belonging to all the classes above mentioned, but there are many others which do not belong to these classes. Considering the power of ammonium salts in general to form complex compounds with metallic salts, one cannot avoid the conclusion that there is some power in nitrogen which makes the formation of these compounds possible. The position of the double halides containing ammonium is certainly exceptional. They seem to be governed by some law of their own." Similarly, while there is, of course, a general analogy between cyanides and halides, it is not surprising that they do not conduct themselves exactly alike in all respects. It should be added, however, that there are a few double halides that correspond in composition to potassium ferrocyanide. These will be discussed further on.

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[1] This Journal **11**, 291.

Ramsay advances three arguments in opposition. These are given below, with a few comments suggested by them:

1. The figures obtained in the determination of the specific gravity of the vapors of aluminium methyl and of aluminium ethyl indicate that at lower temperatures these compounds must be represented by the formulas $Al_2(CH_3)_6$ and $Al_2(C_2H_5)_6$, while, at higher temperatures, they are plainly simpler and probably correspond to the formulas $Al(CH_3)_3$ and $Al(C_2H_5)_3$. This suggests that these compounds are like aluminium chloride which, at lower temperatures, gives figures leading to the formula Al_2Cl_6, while, at higher temperatures, the figures lead to the formula $AlCl_3$. From

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[1] London: I. & A. Churchill, 1891.

[2] Ztschr. physik. Chem. **4**, 270.

these facts it appears that the compound Al_2Cl_6 cannot be explained by assuming that the two molecules $AlCl_3$ are held together by the chlorine atoms, for this same explanation cannot be applied to the case of methyl and ethyl compounds, as they contain no chlorine nor other halogen atoms. Further, as the existence of the complex molecule, Al_2Cl_6, cannot be explained in this way, it follows that the double halides cannot be explained in this way.

This argument cannot be regarded as a strong one, even assuming that the experimental basis is sufficient to justify the premises. It is by no means certain that aluminic chloride at lower temperatures is similar to the double halides. It seems to me probable that it is so, but there are some reasons for thinking that it may not be. The most prominent of these is the fact that the double halides seem to be formed by virtue of a certain oppositeness of character of the uniting halides, just as oxy-salts are formed in consequence, as we say, of the basic and acidic properties of the uniting oxides. In the double compound Al_2Cl_6 we have two molecules of the same kind united. What is the incentive to union in this case? Whatever it may be, it would seem at first sight to be different from that which leads to the formation of the double halides proper. Among oxygen compounds there are cases similar to aluminium chloride, as, for example, arsenious oxide, the specific gravity of whose vapor leads to the formula As_4O_6. No satisfactory explanation of these facts can be offered at present, though it seems to me probable that such compounds are analogous to ordinary salts. We do not hesitate to assume that the oxides Sb_2O_4, Fe_3O_4, Pb_3O_4, etc., are analogous to salts. If this assumption be true, it does not appear that we are violating any fundamental principle of chemistry in assuming that arsenious oxide is of the same order. So also the assumption that aluminium chloride, Al_2Cl_6, is analogous to the double chlorides is not without reason. The question then remains, is this doubled molecule analogous to the methyl and ethyl compounds of aluminium? Professor Ramsay says it is, but Quincke, the latest and by far the most careful experimenter on the organic derivatives of aluminium, thinks not. In an article[1] giving the results of his experiments he uses these words: "Diese Versuche nach dem Gasverdrängungsverfahren geben also keine Bestätigung der Resultate von Louïse und Roux; sie sprechen vielmehr in entschiedener Weise gegen jede Existenz von Gasmolekülen der Form $Al_2(CH_3)_6$. Denn da bereits 10° oberhalb des Siedepunktes die Dichte um 20 per cent. kleiner ist, als der Formel $Al_2(CH_3)_6$ entspricht, so bestehen unzweifelhaft unter den obwaltenden Bedingungen Moleküle von dieser Grösse nicht. Demnach kann die Formel des Aluminiummethyls nur durch $Al(CH_3)_3$ ausgedrückt werden."

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[1] Ztschr. physik. Chem. **3**, 165.

2. Ramsay's second argument is this: "It is impossible to class compounds containing water of crystallisation otherwise than as additive compounds, and there appears no reason to believe that double halides are otherwise constituted" (p. 506). This is simply begging the question. There was a time not long past when to call a substance a "molecular compound" was held to be an explanation. The farther the study of compounds is pushed the less room does there seem to be for molecular or additive compounds. As for myself, I am not prepared to deny the existence of additive compounds as something different from substitutive or atomic compounds, nor, I may add, am I prepared to admit their existence. It seems more probable that, when our knowledge of that property of atoms which we call valence—so important and yet so little understood—shall have been sufficiently extended, we shall see that the existence of all chemical compounds, whether molecular or atomic, is due to the operation of the same cause. This is, of course, worth nothing as an argument, but I think it is worth as much as the opinion expressed by Ramsay.

3. The third argument is this: If the supposition that the double halides are formed "by virtue of the halogen elements, which in such compounds function as *triads* towards each other, . . . it becomes possible to represent any double halides whatever constitutionally. . . . Given the hypothesis, all double halides may be thus represented by a little ingenuity." While the hypothesis referred to does admit the existence of many double halides, it certainly excludes many. It is not true that by means of it any double halides whatever can be represented constitutionally. For example, while the compounds KF.HF, KF.2HF, and KF.3HF, which are known, can be explained, the compound KF.4KF, which is not known, cannot be explained. As well find fault with the law of multiple proportions because it suggests an infinite number of possibilities, or with the valence hypothesis because it can be used to explain many things unknown to man.

There is evidently some law limiting the application of the law of multiple proportions, as there is some law limiting the valence of elements. We first recognise the general truth and then strive to learn what its limitations are.

Since the publication of my first article,[1] investigations have been carried on under my guidance for the purpose of testing the law of composition of the double halides deduced by me from a consideration of the facts. This law as first stated is as follows:

When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter.

This law is based on a study of the composition of between four and five hundred cases. Attention was called, however, to the existence of one exception to the law, viz., the salt $CuCl.2KCl$ or $Cu_2Cl_2.4KCl$. Further examinations of the literature have brought to light a few more exceptions, and the first object of the researches, an account of which follows, was to determine whether the anomalous salts could be obtained or not.

The double halides of tin were investigated by Mr. G. M. Richardson for the purpose of determining whether the salt $SnCl_2.4KCl.3H_2O$, which has been described by Poggiale,[2] exists. It having been found impossible to make this salt, the investigation was pushed in various directions. A number of other double halides of tin were examined, and the work shows that all the salts thus far made conform to the above law.

The double halides of lead were investigated by Mr. C. H. Herty. Several double iodides of lead have been described, and among them one having the composition $K_4PbI_6(PbI_2.4KI)$. This was described by Boullay.[3] Mr. Herty's work proves that this salt cannot be obtained, and, furthermore, that the only double iodide of lead that can be obtained under ordinary conditions is the one having the composition $KPbI_3.2H_2O\ (PbI_2.KI.2H_2O)$. This is the only double iodide obtained by us, though the conditions were modified in every way that the imagination suggested. The investigation showed further that there is a well crystallised salt of the formula $KPbBr_3.H_2O$, and another of the formula $KPbCl_3$. So far as has been determined, then, up to the present, the double halides of lead conform to the law.

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[1] Loc. cit.

[2] Pogg. Ann. **94**, 507.

[3] Ann. chim. phys. [2] **34**, 366.

The study of the double halides of manganese and of some of those of antimony was carried out by Mr. C. E. Saunders. As regards the manganese compounds, they were found to conform to the law in every respect, and, as they were exhaustively studied, it may safely be asserted that there is no exceptional double halide of manganese. Among the antimony compounds there are, however, some very peculiar ones. They are not exceptions to the law, but it must be confessed that they put the hypothesis as to the structure of the double halides to a severe test. Godeffroy[1] has described two peculiar double chlorides of antimony, one containing cæsium and the other rubidium. To these he assigns the formulas $SbCl_3.6CsCl$ and $SbCl_3.6RbCl$. These plainly form marked exceptions to the law, and the results of their investigation were awaited with special interest. Mr. Saunders has shown that these salts have no existence. On the other hand, while the salts found are for the most part comparatively simple, two of them are specially noteworthy. The simpler salts are those represented by the formulas $Cs_3Sb_2Cl_9$, which is the only double chloride of cæsium and antimony, and $RbSbCl_4$. Those of peculiar composition are represented by the formulas $Rb_5Sb_3Cl_{14}$ and $Rb_{23}Sb_{10}Cl_{53}$, or, writing them in the usual way, these formulas are $3SbCl_3.5RbCl$ and $10SbCl_3.23RbCl$. The peculiarity of the composition of these salts led to special precautions in their analysis. The results obtained cannot be brought in harmony with simple formulas. The more complex of these salts is the one most easily obtained and most easily purified. It crystallises beautifully, and its properties are altogether such as to show that we were working with a pure substance. There seems therefore no escape from the conclusion that the salt has the above formula or one very near it. An attempt to express the structure of this salt by means of the hypothesis found so useful in all the other cases thus far discussed showed that the simple conception of a double chlorine atom acting as an oxygen atom is not sufficient, and that to account for this remarkable case it is necessary to assume that three chlorine atoms act together in such a way so as to form a trivalent group. If this salt were the only one necessitating this assumption the suggestion would not be justifiable, but there are a few well-established simple cases which can be accounted for only in this way. There are, for example, the salts $CuCl.2KCl$ and

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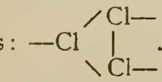
[1] Zeitschr. des allg. österr. Apotheker-Vereins, 1874, 161, and Ber. d. chem. Gesell. 7, 375.

$CdCl_2.4KCl$. The former was first described by Mitscherlich,[1] and a recent examination of the salt by Mr. Richardson in this laboratory has shown that it undoubtedly exists. The latter was described by Von Hauer,[2] and Mr. Richardson has also examined this with the same results. While nearly all double halides conform to the law and are therefore in accordance with the hypothesis of the double halogen atom acting as a bivalent group, there are a few—*not more than three or four out of over four hundred*—that cannot be explained in this way. In these exceptional cases it seems necessary to assume that three halogen atoms acting together form a trivalent group $>(Cl_3)-$, or, assuming that chlorine is trivalent, the group must be represented structurally thus:  $-\mathrm{Cl}\begin{array}{l}\diagup\mathrm{Cl}-\\ \;|\\ \diagdown\mathrm{Cl}-\end{array}$. I am aware that such considerations will not be likely to meet with approval, but let the fact be again emphasised that most double halides have a simple composition, in nearly all cases showing analogy with the corresponding oxygen compounds; that there is nothing indefinite in their composition; that the law governing the composition of nearly all of them is certainly very simple. Let any one carefully study the facts and he will without doubt reach the conviction that in the double halides we have to deal not with the results of the haphazard combination of molecules, but with compounds as definite as any known to us. It cannot be that they should be classed apart.

Mr. C. P. Brigham has studied some of the double halides of bismuth, the investigation having been undertaken principally with the object of determining whether the two salts described by Godeffroy, Rb_6BiCl_9 ($BiCl_3.6RbCl$), and Cs_6BiCl_9 ($BiCl_3.6CsCl$), exist or not. As was expected after the results of the work of Mr. Saunders, these salts cannot be obtained. Bismuth chloride forms, however, three salts with rubidium chloride. These have the following formulas: $RbBiCl_4.H_2O$ ($BiCl_3.RbCl.H_2O$), Rb_3BiCl_6 ($BiCl_3.3RbCl$), and $Rb_{23}Bi_{10}Cl_{53}$ ($10BiCl_3.23RbCl$). The last one has, as will be seen, the same complicated composition as the rubidium salt of antimony chloride already referred to. With cæsium chloride, bismuth chloride forms two salts with the following formulas: Cs_3BiCl_6 ($BiCl_3.3CsCl$), and $Cs_3Bi_2Cl_9$ ($2BiCl_3.3CsCl$). All the above salts conform to the law. Mr. Brigham has also studied a few other double halides of bismuth. On comparing the formulas of the salts containing sodium, potassium, rubidium, and cæsium, a curious and interesting regularity as regards the water of crystallisation is observed. The formulas of the salts are here given: $Na_2BiCl_5.3H_2O$, $K_2BiCl_5.2H_2O$, $RbBiCl_4.H_2O$, and Cs_3BiCl_6. As the atomic weight of the metallic element increases, the number of molecules of water of crystallisation decreases. A similar regularity is observed on comparing the formulas of some of the salts described by Mr. Herty. In the series $KPbI_3.2H_2O$, $KPbBr_3.H_2O$, and $KPbCl_3$, there is a regular decrease in the number of molecules of water of crystallisation. In this series the variable is the halogen, and the amount of water of crystallisation decreases as the atomic weight of the halogen decreases.

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[1] Ann. chim. phys. **73** (1840), 384.

[2] Jour. prak. Chem. **64**, 486.

If the specific gravity of some double halide in the form of vapor could be determined, and the results should be found to accord with those required by the commonly accepted formula, that one at least would be rescued from the slough of "molecular compounds." Accordingly, some efforts have been made to secure such determinations. Landolph[1] states that, when anethol is treated with boron trifluoride, a compound of the formula HBF_4 is formed, and he describes this as boiling at 130° with partial decomposition. Indeed, the author gives the results of the determination of the specific gravity of its vapor, and these results are well in accord with the theory. It is needless to point out the importance of this observation for the whole subject of double halides. Unfortunately, the observation could not be verified. Mr. R. de Roode undertook the repetition of this work. He followed the directions with the greatest care and repeated the experiment a number of times, but only with negative results as far as the main point is concerned. Nothing could be obtained corresponding in properties to the compound described, and we were reluctantly compelled to give up the work, with the conviction that no aid can be obtained from that source.

Again, a compound of sulphur chloride and mercurous chloride has been described by Capitaine.[2] He gave it the formula $SCl_2.Hg_2Cl_2$, and stated that it could be vaporised without decomposition. Mr. J. E. Gilpin has undertaken the preparation and

[1] C. R. **86**, 603.

[2] Journ. de Pharmac. **25**, 566; and Journ. prak. Chem. **18**, 437.

study of this compound. He has found that there is no difficulty in preparing it in any desired quantity; that it is a well crystallised compound of definite composition with the above formula. He has further shown that, as stated by Capitaine, when heated it is converted into vapor and again deposited, apparently unchanged. Careful study has proved, however, that it suffers dissociation under the influence of heat, its constituents recombining when the temperature is lowered. As determinations of the specific gravity of the vapor of a substance conducting itself in this way would be of no value, the determinations were not made.

I hope in the near future to make determinations of the specific gravity of the vapor of the double chloride of aluminium and sodium at different temperatures. Whether such determinations are feasible remains to be seen. From the published accounts of the compound, I judge that work in this line is promising. Deville states[1] that it can be converted into vapor without decomposition. I shall also continue my efforts with other compounds, both with reference to their composition and to the specific gravity of their vapors. The peculiar results obtained in the study of the rubidium salts of antimony and of bismuth chlorides furnish an incentive to the study of other double halides containing rubidium, and such work will be undertaken here. Mr. H. C. Jones is at present engaged in the study of the double halides of gold, and, in the course of this investigation, we propose to examine the salts containing rubidium.

The detailed accounts of the investigations referred to in this general account are given below.

I.—ON THE DOUBLE HALIDES OF TIN.[2]

BY GEORGE M. RICHARDSON.

Compounds of Stannous Chloride and Potassium Chloride.

Poggiale[3] has described a salt of the formula $SnCl_2.4KCl.3H_2O$. In addition to this salt, one of the composition $SnCl_2.2KCl$ is recorded, but there seems to be some confusion regarding it.

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[1] Ann. ch. phys. [3], **43**, 25.

[2] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1890.

[3] Pogg. Ann. **94**, 507.

Graham gives it the formula $SnCl_2.2KCl.3H_2O$; Mitscherlich in his text-book speaks of the salt $SnCl_2.2KCl.2H_2O$; Apjohn describes the salt $SnCl_2.2KCl.H_2O$ and states that it crystallises in octahedra. Rammelsberg has analysed[1] and measured[2] an orthorhombic salt to which he assigns the formula $SnCl_2.2KCl.H_2O$, and says further that the octahedra obtained by Apjohn were probably the stannic salt $SnCl_4.2KCl$. This salt is frequently formed along with stannous salt. Marignac[3] confirmed the results of Rammelsberg.

The double halides here described were prepared, in most cases, by mixing the solutions of the constituent halides. The alkaline halide was dissolved in water, and the tin solution was made by dissolving tin in hydrochloric acid or hydrobromic acid, an excess of tin being present to prevent the presence of free acid in the solution.

Mono-potassium chloro-stannite, $KSnCl_3.H_2O$.—When a solution of potassium chloride is mixed with a solution of stannous chloride in such proportions that the stannous chloride is present in large excess, white, hair-like crystals will form after a time, or, if the solutions are nearly saturated, at once. These crystals, carefully dried by pressing between drying papers, were analysed with the following results:

	Found.	Calculated.
Sn	41.60 per cent.	41.91 per cent.
K	14.09	13.88
Cl	38.15	37.82
H_2O	5.88	6.39
	99.72	100.00

From which it appears that the formula is $SnCl_2KCl.H_2O$ or $KSnCl_3.H_2O$.

This salt is quite stable in the air; it does not lose its water of crystallisation over sulphuric acid, but loses it at 100°, without suffering further change. Heated to high temperatures it loses hydrochloric acid with its water of crystallisation, and is thus decomposed, oxides of tin being formed. The salt is decomposed by water, forming a turbid solution; it dissolves, forming a clear solution, in hot hydrochloric acid or in a hot solution of potassium chloride, but from both of these solutions there crystallises out on cooling a salt having the composition $SnCl_2.2KCl.2H_2O$ or $K_2SnCl_4.2H_2O$.

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[1] Pogg. Ann. **94**, 507.

[2] Krystal. Chemie, p. 211.

[3] Jahresber. 1857, 221.

Di-potassium chloro-stannite, $K_2SnCl_4.2H_2O$.—If, instead of having the stannous chloride present in large excess, the solutions are mixed in about equal portions or the potassium chloride is present in excess, large, opaque, white, orthorhombic crystals are formed after standing for a time. The crystals, carefully dried and analysed, gave the following results:

	Found.		Calculated.
	A.	B.	
Sn	31.54 per cent.	31.46 per cent.	31.55 per cent.
K	20.64	21.48	20.86
Cl	38.54	37.59	37.97
H_2O	9.37	10.47	9.62
	100.09	101.00	100.00

These results show that the formula is $K_2SnCl_4.2H_2O$. This salt is perfectly stable in the air. A sample which had been exposed to the action of the atmosphere for forty days gave with ferric chloride and standard permanganate solution 31.49 per cent. of stannous tin, the theory being 31.55 per cent. It does not lose its water of crystallisation over sulphuric acid, but gradually loses the whole of it at 100° without change. It can be recrystallised without change from hydrochloric acid, being quite soluble in the hot acid and comparatively insoluble in the cold acid. It can also be recrystallised from a potassium chloride solution without change of composition. The habit of the crystals formed in the two cases is quite different; from the hydrochloric acid they are much elongated, parallel to the C axis, and rarely have terminal planes, while from the potassium chloride solution they are less elongated and the terminal planes are well formed.

Di-potassium chloro-stannite, $K_2SnCl_4.H_2O$.—When large quantities of the salt just described, $K_2SnCl_4.2H_2O$, are dissolved in hot hydrochloric acid and the solution quickly cooled, a white crystalline precipitate is formed, and after a few moments crystals of the salt $K_2SnCl_4.2H_2O$ begin to grow, and increase in size with great rapidity. If the crystalline precipitate is removed before the crystals of the second salt begin to form, and is analysed, it is found to have the formula $K_2SnCl_4.H_2O$, that is, it differs by one molecule of water of crystallisation from the large crystals.

The following results were obtained by analysis:

	Found.	Calculated.
Sn	33.05 per cent.	33.15 per cent.
K	21.48	21.91
Cl	39.11	39.89
H_2O	...	5.05
		100.00

This salt also is stable in the air, but if left in its mother-liquor it gradually takes up more water of crystallisation and is transformed into the salt $K_2SnCl_4.2H_2O$. It does not lose its water of crystallisation over sulphuric acid, but loses it at 100°. If this salt or the one with two molecules of water be dissolved in hot stannous chloride solution, the salt $KSnCl_3.H_2O$, already described, crystallises out on cooling.

All efforts to prepare other salts composed of stannous chloride and potassium chloride than those just described have proved fruitless. The salt $K_2SnCl_4.2H_2O$ was dissolved in potassium chloride solution in the hope of getting the salt described by Poggiale, but in vain; the salt $K_2SnCl_4.2H_2O$ was again obtained and the excess of potassium chloride crystallised out by itself.

The solutions were mixed so that a large excess of potassium chloride was present, but with the same result, the potassium chloride in excess of that required for the salt $K_2SnCl_4.2H_2O$ crystallised out alone, for the most part in transparent octahedra.

The mother-liquors from these crystals were evaporated and a second and third crop of crystals obtained, but always with the same result. By the evaporation there were also formed octahedra of the well-known stannic salt K_2SnCl_6 or $SnCl_4.2KCl$, since the evaporation of the solutions oxidises the tin.

When a saturated solution of stannous chloride is added to a saturated solution of potassium chloride, crystals form very rapidly, and so completely fill the liquid in a few moments that it can be inverted without loss of the solution. An examination of this mass proves it to consist of all three of the salts above described, but upon standing a few days, if sufficient potassium chloride is present, it will be entirely converted into the salt $K_2SnCl_4.2H_2O$, otherwise there will remain a mixture of the two salts $K_2SnCl_4.2H_2O$ and $KSnCl_3.H_2O$; the latter salt appears to be stable only in the presence of a considerable excess of stannous chloride if allowed to remain in the solution from which it has crystallised. So also, as we have seen, the salt $K_2SnCl_4.H_2O$ will take up an additional molecule of water if it be allowed to stand in its mother-liquor for several days; but if it be removed before long standing it is possible to get a mass of crystals of $K_2SnCl_4.2H_2O$, which are in a matrix of the salt $K_2SnCl_4.H_2O$.

Compounds of Stannous Chloride and Ammonium Chloride.

Mono-ammonium chloro-stannite, $NH_4SnCl_3.H_2O$.—This salt is prepared just as the corresponding potassium salt and, as far as determined, it is analogous to the potassium salt in every respect, with the exception that the tendency to pass over into the orthorhombic form is here even more marked than in the case of the potassium salt.

Di-ammonium chloro-stannite, $(NH_4)_2SnCl_4.2H_2O$.—This salt is very readily obtained by bringing the solutions of the component chlorides together and allowing them to stand. It is isomorphous with the corresponding potassium salt, which it resembles in its general properties. The tin and water were determined in this salt with the following results:

	Found.	Calculated.
Sn	35.54 per cent.	35.58 per cent.
H_2O	9.95	10.84

This analysis proves its formula to be $(NH_4)_2SnCl_4.2H_2O$.

All efforts to prepare the salt with one molecule of water of crystallisation, $(NH_4)_2SnCl_4.H_2O$, analogous to the potassium salt $K_2SnCl_4.H_2O$, have been unsuccessful.

Crystals of the salt $(NH_4)_2SnCl_4.2H_2O$ and of the salt $K_2SnCl_4.2H_2O$ have been measured[1] and they are found to be the same as those measured by Rammelsberg,[2] yet he ascribes to them the composition represented by the formulæ $(NH_4)_2SnCl_4.H_2O$ and $K_2SnCl_4.H_2O$. For the potassium salt he gives the following analysis:[3]

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[1] See crystallographic measurements, pages 101–103 of this paper.

[2] In his Krystal. Chemie, 211 and 212.

[3] Pogg. Ann. **94**, 510.

	Found. A.	Found. B.	Calculated.
K	23.07 per cent.	22.79 per cent.	22.00 per cent.
Sn	33.32	33.58	33.07
Cl	...	...	39.87
H_2O	...	...	5.06

From these results it would appear that Rammelsberg had measured one salt and analysed another. This is not improbable, since they may both occur in the same crystal mass.

But how is it with regard to the ammonium salt? We have seen that the ammonium salt with one molecule of water of crystallisation cannot be prepared, so that it would be impossible to make a similar mistake here.

He obtained by analysing his ammonium salt the following results:[1]

	Found.	Calculated.
NH_4	10.24 per cent.	11.49 per cent.
Sn	35.93	37.52
Cl	44.39	45.25
H_2O	...	5.74

On the basis of this analysis he assigned to the salt the formula $(NH_4)_2SnCl_4.H_2O$. But the calculated results for the formula with two molecules of water are:

NH_4	10.84 per cent.
Sn	35.54
Cl	42.78
H_2O	10.84
	100.00

These calculated results agree more closely with Rammelsberg's analysis than do the results calculated from the formula which he assigns to the salt, so that his own analysis proves that the formula for the ammonium compound at least is $(NH_4)_2SnCl_4.2H_2O$ and not $(NH_4)_2SnCl_4.H_2O$.

Poggiale in describing the salts $SnCl_2.4KCl.3H_2O$ and $SnCl_2.4NH_4Cl.3H_2O$ gives no analyses, but says that the salts were obtained directly from a mixture of the solutions in beautiful long needles. The salts he obtained were in all probability K_2SnCl_4.

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[1] Loc. cit.

$2H_2O$ and $(NH_4)_2SnCl_4.2H_2O$, or as they are usually written $SnCl_2.2KCl.2H_2O$ and $SnCl_2.2NH_4Cl.2H_2O$.

The Action of Stannous Chloride upon Sodium Chloride and Lithium Chloride.—If saturated solutions of stannous chloride and sodium chloride be mixed no crystals are formed. If the solution be evaporated or allowed to stand over sulphuric acid for a long time the solution becomes thick and oily, and finally after the volume of the liquid has been much reduced sodium chloride crystallises out alone.

Lithium chloride behaves in the same way.

Compounds of Stannous Bromide and Potassium Bromide.

Very little is said of these compounds in the literature. They are spoken of only in connection with the chlorides, and are said to be similar to them.

Mono-potassium bromo-stannite, $KSnBr_3.H_2O$.—On adding a solution of potassium bromide to a solution of stannous bromide, bundles of long hair-like crystals are formed almost instantly, if the solutions are concentrated, and these grow with great rapidity until the vessel is quite filled with them. These crystals were analysed with the following results:

	Found.	Calculated.
Sn	27.77 per cent.	28.43 per cent.
H_2O	4.35	4.34

This salt is similar in appearance to the corresponding chloride, and like it is quite stable in the air, retains its water of crystallisation over sulphuric acid, but loses it at 100° without change of the salt. But it differs from the chloride in being much more readily formed from the mixed solutions, being formed even in the presence of an excess of potassium bromide. It can be recrystallised from hydrobromic acid, and even from a solution of potassium bromide.

Di-potassium bromo-stannite, $K_2SnBr_4.2H_2O$.—As just seen, when solutions of stannous bromide and potassium bromide are mixed the salt $KSnBr_3.H_2O$ is always formed, but if there is present an excess of potassium bromide, or if the salt $KSnBr_3.H_2O$ is dissolved in a solution of potassium bromide, and the crystals which separate out on cooling are allowed to stand several days in the solution, it will be found that large orthorhombic crystals are scattered through the mass of other crystals.

This salt is similar to the corresponding chloride in its general appearance and in its properties. An analysis of the crystals led to the results that follow, proving its formula to be $K_2SnBr_4.2H_2O$.

	Found.	Calculated.
Sn	21.08 per cent.	21.38 per cent.
H_2O	6.12	6.52

The salt cannot be recrystallised from its solutions in hydrobromic acid; if it is dissolved in this acid the salt $KSnBr_3.H_2O$ crystallises out. A salt with one molecule of water of crystallisation analogous to the chloride $K_2SnCl_4.H_2O$ was not obtained.

Compounds of Stannous Bromide and Ammonium Bromide.

Mono-ammonium bromo-stannite, $NH_4SnBr_3.H_2O$.—On mixing the solutions of stannous bromide and ammonium bromide hair-like crystals of $NH_4SnBr_3.H_2O$ are at once formed. In its general properties this salt is like other analogous salts already described; it differs from the corresponding chloride, $NH_4SnCl_3.H_2O$, in that it is much more readily formed from the mixed solutions, and it differs from the corresponding potassium salt, $KSnBr_3.H_2O$, in being less readily formed from the mixed solutions, and in passing more readily over into the orthorhombic variety.

Di-ammonium bromo-stannite, $(NH_4)_2SnBr_4.2H_2O$.—Crystals of this salt are obtained by mixing the two solutions so that ammonium bromide is present in excess, and allowing the salt $NH_4SnBr_3.H_2O$, which is at first formed, to stand. It resembles the other corresponding salts already described. Analyses of the crystals gave:

	Found.		Calculated.
	A.	B.	
Sn	23.00 per cent.	22.97 per cent.	23.14 per cent.
H_2O	6.34		7.06

Crystals of this salt are more readily obtained than the crystals of the salt $K_2SnBr_4.2H_2O$, but are not so easily obtained as either of the chlorides $K_2SnCl_4.2H_2O$ or $(NH_4)_2SnCl_4.2H_2O$.

Compounds containing Chlorine and Bromine.

Compounds of Stannous Bromide with Potassium Chloride.—When a solution of potassium chloride is added to a solution of stannous bromide, hair-like crystals are formed, just as when the two chlorides or the two bromides are mixed, and it was thought from the analogy that the salt $KSnBr_2Cl.H_2O$ or $SnBr_2KCl.H_2O$

was formed, but on analysis it was found not to yield constant results. Several specimens of this salt were prepared, and the tin was determined with the following results:

Sample A gave 28.63 per cent. Sn.
" B " 29.66
" C " 31.19
" D " 30.04
" E " 29.21.

The calculated percentage of tin in a salt having the formula $\mathrm{SnBr_2KCl.H_2O}$ is 31.84 per cent. Possibly different salts are formed as follows:

$$\mathrm{4SnBr_2 + 4KCl + 4H_2O} = \left\{ \begin{array}{ll} \mathrm{SnBr_2KBrH_2O} & (1) \\ \mathrm{2)SnBr_2KClH_2O} & (2). \\ \mathrm{SnCl_2KBrH_2O} & (3) \end{array} \right.$$

The calculated amounts of tin in these salts are, (1) 28.43 per cent.; (2) 31.84 per cent.; (3) 36.18 per cent.

Or, more probably, it is a mixture of the two salts $\mathrm{KSnBr_3.H_2O}$ and $\mathrm{KSnCl_3.H_2O}$, the former being present in excess, as we should expect, since we have seen that it is much more readily formed than the latter. The percentage of tin in these two salts is:

$$\mathrm{KSnBr_3.H_2O} = 28.43$$
$$\mathrm{KSnCl_3.H_2O} = 41.91.$$

In order to decide this point, further investigation is necessary.

A similar mixture is obtained when potassium bromide solution is added to stannous chloride solution. The same is true of solutions of ammonium chloride and stannous bromide, or of ammonium bromide and stannous chloride. When the alkaline halide is added in excess, orthorhombic crystals are formed.

An analysis of some of the crystals formed by adding potassium chloride to stannous bromide led to the formula $\mathrm{K_2SnCl_2Br_2.2H_2O}$. The results of the two analyses are as follows:

	Found.		Calculated.
	A.	B.	
Sn	25.63 per cent.	25.48 per cent.	25.49 per cent.
K	17.21	17.17	16.85
Br	36.60	36.70	34.56
Cl	15 46	14.94	15.33
H_2O	4.60	...	7.77
	99.50		100.00

Similar crystals were made by mixing the solutions of stannous chloride and potassium bromide, and these were analysed with the following results:

	Found.
Sn	24.18 per cent.
K	16.66
Br	34.43
Cl	15.27
H_2O	8.01
	98.55

which leads to the same formula, $K_2SnCl_2Br_2.2H_2O$, as assigned to the crystals prepared from stannous bromide and potassium chloride. These crystals could not be distinguished from one another in any way.

These crystals, when heated in a current of dry air, first lose water with some hydrochloric acid and some hydrobromic acid, with the formation of oxychloride and oxybromide of tin; then stannous chloride and stannous bromide sublime and are deposited in the cooler parts of the tube, leaving behind a mixture of potassium chloride, potassium bromide, tin oxychloride, and tin oxybromide. If the water be first driven off at 100° and the dried salt heated in a current of dry hydrogen, the stannous bromide and chloride sublime, leaving potassium bromide and chloride behind. There is also a slight reduction of the tin to the metallic state, and both hydrochloric and hydrobromic acids are given off.

The angles of these two series of crystals appear to be the same, but the faces gave such poor reflections and so many images that accurate measurements could not be made. With the hope of getting better crystals, several more specimens of the salt were prepared from solutions of different strengths. Upon analysis these new specimens were found to contain varying amounts of tin. Six specimens gave respectively 25.04, 25.71, 26.02, 26.59, 27.34, and 26.94 per cent. of tin.

The faces of these crystals also gave poor reflections and multiple images, yet a variation in angle could be detected in the crystals of different composition.

In the case of the ammonium salt the reflections are much better and the crystals can be very accurately measured. The crystals from different solutions are found to vary in their angles, and upon analysis are found to be of variable composition. A determination of tin in four different specimens resulted as follows: 24.29, 24.42, 25.20, and 25.56 per cent. of tin.

The calculated amount of tin in a compound having the formula $(NH_4)_2SnBr_2Cl_2.2H_2O$ is 28.03 per cent. These results suggest that we have here to deal with an isomorphous mixture of the chloride and the bromide. If this be the case it ought to be possible to get crystals varying in their percentage of tin from 21.38 per cent. in the case of the pure salt $K_2SnBr_4.2H_2O$ to 31.55 per cent. in the case of the pure salt $K_2SnCl_4.2H_2O$, and from 23.14 per cent. to 35.55 per cent. in the case of the ammonium salts. A further study of these salts will be carried out in order to determine the amount of change in angle measurement that accompanies a given change in composition, and to decide, if possible, whether or not the molecule $K_2SnCl_2Br_2.2H_2O$ exists.

R. W. Atkinson[1] has prepared the salt $K_3SbCl_3Br_3.1\frac{1}{2}H_2O$ by mixing antimony chloride and potassium bromide, and the same salt by mixing potassium chloride with antimony bromide. And R. H. Solly[2] has proved their crystallographic identity. Atkinson also obtained crystals to which he gives the formula $Sb_2Cl_6Br_3K_3.2H_2O$ and $SbCl_3BrK.H_2O$; he does not speak of having any difficulty in obtaining pure specimens.

Summary of the Results.

It is clear, then, that stannous chloride and bromide form two classes of salts with potassium and ammonium bromide and chloride. One class contains one molecule of the alkaline halide, and the other class contains two molecules of the alkaline halide. In the case of the chlorides the tendency to form the salt with two molecules of the alkaline chloride is very strong, and is even more marked with the ammonium chloride than with the potassium chloride. With the bromides on the other hand the tendency is to form the salt with one molecule of the alkaline bromide, while the one with two molecules of the alkaline bromide is obtained with greater difficulty, and here too the salt with two molecules of ammonium bromide is much more readily obtained than the potassium salt.

The salts of lithium and sodium, if formed at all, are so soluble that they cannot be crystallised.

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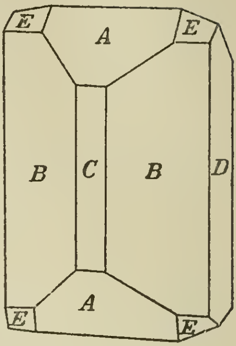
[1] Jour. Chem. Soc. **43** (1883), 289.

[2] Ibid. 293.

Crystallographic Examination of Salts.

We have seen that the salts $K_2SnCl_4.2H_2O$, $(NH_4)_2SnCl_4.2H_2O$, $(NH_4)_2SnBr_4.2H_2O$, $K_2SnBr_4.2H_2O$ are all orthorhombic in their crystallisation and that they have the same habit, the most general form being that shown in the figure, in which

$A = P\bar{\infty}$
$B = \infty P$
$C = \infty P\bar{\infty}$
$D = \infty P\breve{\infty}$
$E = P$



Most of the crystals consist simply of the two forms ∞P and $P\bar{\infty}$, others are modified by $\infty P\bar{\infty}$ and $\infty P\breve{\infty}$ and rarely P. The salt $K_2SnBr_4.2H_2O$, however, rarely has the $P\bar{\infty}$ developed, but is terminated by P instead.

In the following observations the faces of the crystals are classified as *poor* (p), *fair* (f), *good* (g), *very good* (v. g.) according to the clearness of the reflected image which they give. In making up the means of the observations the different observations were given different weight according to the perfectness of the reflected image.

The following weights were assigned to the different observations:

2 poor images have a weight of 1.
1 poor image and 1 fair image have a weight of 2.
1 poor image and 1 good image have a weight of 3.
1 poor image and 1 very good image have a weight of 4.
2 fair images have a weight of 5.
1 fair image and 1 good image have a weight of 6.
1 fair image and 1 very good image have a weight of 7.
2 good images have a weight of 8.
1 good image and 1 very good image have a weight of 9.
2 very good images have a weight of 10.

The means where each observation has the same weight are also calculated for comparison.

But for calculation of the axial ratios the numbers obtained by the use of weights were taken in every case.

Measurements of Di-potassium Chloro-stannite, $K_2SnCl_4.2H_2O$.

Obtuse prism angle, B to B over C.

Crystal measured.	Weight of observation.	Observed angle.	Calculated angle and differences.
			111° 9′ 35″
No. 2, 2 f.	5	111° 13′ 30″	+ 3 55
No. 3, 2 v. g.	10	111 10 30	+ 0 55
No. 4, 2 f.	5	111 11 00	+ 1 25
No. 8, 2 f.	5	111 6 30	− 3 05
No. 11, 1 v. g. and 1 g.	9	111 7 30	− 2 05
Mean,		111 9 48	+ 0 13
Mean with weights,		111 9 36	+ 0 01

Acute prism angle, B to B over D.

			68° 50′ 25″
No. 3, 1 v. g. and 1 g.	9	68° 49′ 00″	− 1 25
No. 5, 1 g. and 1 f.	6	68 51 00	+ 0 35
No. 6, 2 g.	8	68 49 30	− 0 55
No. 8, 2 f.	5	68 51 30	+ 1 05
No. 9, 2 g.	8	68 51 00	+ 0 35
No. 11, 2 v. g.	10	68 51 00	+ 0 35
Mean,		68 50 30	+ 0 05
Mean with weights,		68 50 25	0 00

Angle of macrodome, A to A over top.

			84° 10′ 46″
No. 6, 1 v. g. and 1 f.	7	84° 12′ 00″	+ 1 14
No. 7, 1 g. and 1 p.	3	84 6 00	− 4 46
No. 8, 1 v. g. and 1 f.	7	84 11 00	+ 0 14
No. 9, 1 v. g. and 1 g.	9	84 10 30	− 0 16
No. 11, 2 g.	8	84 11 30	+ 0 44
Mean,		84 10 12	− 0 34
Mean with weights,		84 10 46	0 00

Angle from prism to macropinacoid, B to C.

			145° 34′ 48″
No. 2, 2 g.	8	145° 37′ 30″	+ 2 42
No. 3, 1 v. g. and 1 g.	9	145 35 30	+ 0 42
No. 5, 2 p.	1	145 29 00	− 5 48
No. 9, 1 f. and 1 p.	2	145 37 00	+ 2 12
No. 11, 1 v. g. and 1 p.	4	145 36 00	+ 1 12
Mean,		145 35 00	+ 0 12
Mean with weights,		145 36 06	+ 1 18

Angle from prism to brachypinacoid, B to D

			124° 25′ 12″
No. 3, 1 v. g. and 1 g.	9	124° 24′ 30″	— 0 42
No. 4, 1 f. and 1 p.	2	124 28 00	+ 2 48
No. 6, 1 v. g. and 1 g.	9	124 23 30	— 1 42
No. 8, 2 f.	5	124 25 00	— 0 12
No. 9, 2 g.	8	124 24 00	— 1 12
No. 11, 1 v. g. and 1 g.	9	124 25 30	+ 0 18
Mean,		124 25 05	— 0 07
Mean with weights,		124 24 38	— 0 34

Angle from prism to macrodome, B to A.

			127° 44′ 47″
No. 3, 2 v. g.	10	127° 46′ 00″	+ 1 13
No. 4, 1 f. and 1 p.	2	127 43 30	— 1 17
No. 6, 1 g. and 1 f.	6	127 43 30	— 1 17
No. 8, 2 v. g.	10	127 43 00	— 1 47
No. 9, 2 f.	5	127 43 00	— 1 47
No. 11, 2 v. g.	10	127 44 30	— 0 17
Mean,		127 43 55	— 0 52
Mean with weights,		127 44 08	— 0 39

From the angles 68° 50′ 25″ and 84° 10′ 46″ the value of the axes may be calculated, and the axial ratio is found to be

a : b : c as 0.685231 : 1 : 0.758634.

Measurements of Di-ammonium Chloro-stannite, $(NH_4)_2SnCl_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 39′ 30″
No. 15, 2 p.	1	111° 37′ 00″	— 2 30
No. 16, 2 p.	1	111 43 00	+ 3 30
No. 19, 2 p.	1	111 39 00	— 0 30
No. 20, 2 f.	5	111 39 00	— 0 30
No. 21, 1 v. g. and 1 f.	7	111 39 00	— 0 30
No. 20, 2 f.	5	111 40 30	+ 1 00
Mean,		111 39 35	+ 0 05
Mean with weights,		111 39 28	— 0 02

Acute prism angle, B to B over D.

			68° 20′ 30″
No. 13, 2 f.	5	68 21′ 30″	+ 1 00
No. 15, 2 f.	5	68 23 00	+ 2 30
No. 16, 2 p.	1	68 21 00	+ 0 30
No. 17, 2 p.	1	68 22 30	+ 2 00
No. 18, 2 p.	1	68 25 00	+ 4 30
No. 19, 2 f.	5	68 27 00	+ 6 30
No. 20, 2 f.	5	68 20 30	0 00
No. 21, 2 v. g.	10	68 16 00	— 4 30
Mean,		68 22 04	+ 1 34
Mean with weights,		68 20 27	— 0 03

Angle of macrodome, A to A over top.

			84° 7′ 43″
No. 13, 1 g. and 1 p.	3	84° 11′ 00″	+3 17
No. 15, 2 f.	5	84 11 00	+3 17
No. 16, 1 f. and 1 p.	2	84 05 00	—2 43
No. 17, 1 g. and 1 p.	3	84 09 00	+1 17
No. 19, 2 f.	5	84 07 00	—0 43
No. 20, 1 v. g. and 1 f.	7	84 07 00	—0 43
No. 21, 2 f.	5	84 04 30	—3 13
Mean,		84 07 47	+0 04
Mean with weights,		84 07 43	0 00

Angle from prism to brachypinacoid, B to D.

			124° 10′ 15″
No. 13, 2 f.	5	124° 13′ 30″	+ 3 15
No. 15, 2 f.	5	124 13 00	+ 2 45
No. 16, 2 p.	1	124 12 30	+ 2 15
No. 17, 2 p.	1	124 13 00	+ 2 45
No. 18, 1 g. and 1 p.	3	124 12 30	+ 2 15
No. 19, 1 v. g. and 1 f.	7	124 05 00	— 5 15
No. 20, 1 v. g. and 1 f.	7	124 09 00	— 1 15
Mean,		124 11 13	+ 0 58
Mean with weights,		124 10 07	— 0 08

Angle from prism to macrodome, B to A.

			127° 53′ 46″
No. 15, 1 g. and 1 f.	6	127° 55′ 30″	+ 1 44
No. 16, 2 f.	5	127 55 30	+ 1 44
No. 17, 1 f. and 1 p.	2	127 55 00	+ 1 14
No. 19, 1 f. and 1 p.	2	127 57 00	+ 3 14
No. 20, 2 v. g.	10	127 52 00	— 1 46
Mean,		127 55 00	+ 1 14
Mean with weights,		127 54 11	+ 0 25

The axes may be calculated from the angles 68° 20′ 30″ and 84° 07′ 43″.

The axial ratio is : a : b : c as 0.678855 : 1 : 0.752244.

Measurements of Di-ammonium Bromo-stannite, $(NH_4)_2SnBr_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 43′ 14″
No. 23, 2 f.	5	111° 43′ 00″	— 0 14
No. 24, 2 f.	5	111 41 00	— 2 14
No. 25, 2 f.	5	111 46 00	+ 2 46
No. 26, 2 f.	5	111 41 00	— 2 14
No. 27, 2 f.	5	111 40 00	— 3 14
No. 28, 1 g. and 1 f.	6	111 45 00	+ 1 46
Mean,		111 42 40	— 0 34
Mean with weights,		111 42 44	— 0 30

Acute prism angle, B to B over D.

			68° 16′ 46″
No. 23, 2 f.	5	68° 15′ 00″	— 1 46
No. 24, 2 p.	1	68 18 00	+ 1 14
No. 25, 2 f.	5	68 17 30	+ 0 44
No. 26, 1 f. and 1 p.	2	68 13 30	— 3 16
No. 27, 2 f.	5	68 19 30	+ 2 44
No. 28, 2 f.	5	68 15 00	— 1 46
Mean,		68 16 00	— 0 36
Mean with weights,		68 16 16	— 0 30

Angle of macrodome, A to A over top.

			84° 17′ 42″
No. 23, 1 v. g. and 1 p.	4	84 ′ 30″	+ 2 48
No. 25, 2 g.	8	84 21 00	+ 3 18
No. 26, 2 g.	8	84 20 00	+ 2 18
No. 28, 2 f.	5	84 18 00	+ 0 18
No. 29, 2 v. g.	10	84 21 00	+ 3 18
No. 30, 2 g.	8	84 15 30	— 2 12
No. 31, 1 v. g. and 1 g.	9	84 14 00	— 3 42
No. 32, 2 g.	8	84 16 30	— 1 12
No. 33, 2 g.	8	84 14 00	— 3 42
Mean,		84 17 50	+ 0 08
Mean with weights,		84 17 42	0 00

Angle from the prism to the macrodome, B to A.

			127° 51′ 15″
No. 23, 1 v. g. and 1 p.	4	127° 54′ 00″	+ 2 45
No. 26, 1 g. and 1 p.	3	127 51 30	+ 0 15
No. 27, 2 f.	5	127 53 00	+ 1 45
No. 28, 2 f.	5	127 51 00	— 0 15
No. 29, 1 v. g. and 1 f.	7	127 51 00	— 0 15
No. 30, 2 g.	8	127 51 00	— 0 15
Mean,		127 51 55	+ 0 40
Mean with weights,		127 51 47	+ 0 32

Calculating the axial ratios from the angles 68° 16′ 46″ and 84° 17′ 42″, we have a : b : c as 0.678063 : 1 : 0.749178.

Measurements of Di-potassium Bromo-stannite, $K_2SnBr_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 20′ 52″
No. 34, 2 f.	5	111° 21′ 00″	+ 0 08
No. 35, 2 p.	1	111 20 00	— 0 52
No. 36, 1 f. and 1 p.	2	111 16 00	— 4 52
No. 37, 1 f. and 1 g.	6	111 18 30	— 2 22
No. 38, 2 f.	5	111 24 00	+ 3 08
No. 39, 2 f.	5	111 20 00	— 0 52
No. 40, 1 f. and 1 p.	2	111 20 00	— 0 52
Mean,		111 19 59	— 0 53
Mean with weights,		111 20 12	— 0 40

Acute prism angle, B to B over D.

			68° 39′ 08″
No. 34, 1 f. and 1 p.	2	68° 35′ 00″	— 4 08
No. 36, 1 f. and 1 g.	6	68 45 30	+ 6 22
No. 37, 1 f. and 1 p.	2	68 40 30	+ 1 22
No. 38, 2 f.	5	68 36 00	— 3 08
No. 39, 1 v. g. and 1 g.	9	68 36 00	— 3 08
No. 41, 2 f.	5	68 38 30	— 0 38
No. 42, 2 p.	1	68 40 00	+ 0 52
Mean,		68 38 34	— 0 34
Mean with weights,		68 38 28	— 0 40

Angle of macrodome, A to A over top.

			84° 52′ 46″
No. 37, 2 p.	1	84° 48′ 00″	— 4 46
No. 39, 1 f. and 1 g.	6	84 54 00	+ 1 14
No. 42, 2 f.	5	84 53 00	+ 0 14
Mean,		84 51 40	— 1 06
Mean with weights,		84 53 05	+ 0 19

Angle from prism to pyramid, B to E.

			142° 56′ 48″
No. 37, 2 p.	1	142° 55′ 30″	− 1 18
No. 38, 2 p.	1	143 01 00	+ 4 12
No. 39, 1 f. and 1 g.	6	142 52 30	− 3 18
No. 40, 2 f.	5	143 01 00	+ 4 12
No. 42, 2 p.	1	142 54 00	− 2 18
No. 43, 2 p.	1	142 55 00	− 1 18
Mean,		142 56 45	− 0 03
Mean with weights,		142 56 48	0 00

Calculating the value of the axes from the angles 68° 39′ 08″ and 142° 56′ 48″ we get:

a : b : c as 0.682822 : 1 : 0.746746.

Collecting these results we have the following tabular statement:

	A.	C.	$\infty P \wedge \infty P$.	$P\bar{\infty} \wedge P\bar{\infty}$.
$K_2SnCl_4.2H_2O$	0.685231	0.758634	68° 50′ 25″	84° 10′ 46″
$(NH_4)_2SnCl_4.2H_2O$	0.678855	0.752244	68 20 30	84 07 43
$(NH_4)_2SnBr_4.2H_2O$	0 678063	0.749178	68 16 46	84 17 42
K_2SnBr_4 $2H_2O$	0.682822	0.746746	68 39 08	84 52 46

The changes in the value of the axes may be farther tabulated as follows:

In passing	The change in A is	The change in C is
From $K_2SnCl_4.2H_2O$ to $K_2SnBr.2H_2O$	−0.002409	−0.011888
From $(NH_4)_2SnCl_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$	−0.000792	−0.003066
From $K_2SnCl_4.2H_2O$ to $(NH_4)_2SnCl_4.2H_2O$	−0.006376	−0.006390
From $K_2SnBr_4.2H_2O$ to $(NH_4)_2SnBr_4$ $2H_2O$	−0.004759	+0.002432

From this table we see that the change in the halogen or acid element appears to affect the vertical axis much more than it does the lateral axis, and that the change is much less marked with the ammonium salt than with the potassium salt.

While the change in the alkali or basic element affects both axes to nearly the same extent in the case of the chlorides, and the lateral axis more in the case of the bromides, we find that the vertical axis is *increased* instead of diminished in passing from

$K_2SnBr_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$. The A and C axes are both nearer unity in the chlorides than in the bromides, and in general the potassium salts approach the regular form more closely than the ammonium salts.

It is hoped to increase the number of salts in this series by preparing the rubidium and cæsium salts if possible; with the additional data thus obtained, perhaps the law governing the change in the axes will be more apparent.

II.—ON THE DOUBLE HALIDES OF LEAD.[1]

BY CHARLES H. HERTY.

Several double iodides of lead are described in chemical literature. Boullay[2] describes two. One of these has the composition $KPbI_3$ ($PbI_2.KI$), and the other K_4PbI_6 ($PbI_2.4KI$). In Graham-Otto's Lehrbuch der anorganischen Chemie (Bd. II, 3, p. 1189), a salt of the composition K_5PbI_7 ($PbI_2.5KI$) is mentioned. This seems, however, to be an error of the compiler of the book, as a careful search through the literature has failed to bring to light a salt of this composition. Ditte[3] describes a salt of the composition $K_2PbI_4.4H_2O$; and later Berthelot[4] gives an account of two salts of the composition $K_2PbI_4.2H_2O$ and $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$). Berthelot ascribes the latter salt to Boullay, but no account of this salt could be found in the articles of Boullay. Very little work has been done on other double halides of lead. Reference will be made below to a few articles bearing on this subject.

One of the chief difficulties encountered in this investigation was the analysis of the compounds. It was found at the outset that the methods hitherto used, and those that first suggest themselves, are not capable of yielding satisfactory results. Previous investigators mention no difficulties, and give no directions for analysis. This makes it appear probable that they used methods that cannot give good results. In spite of long continued efforts it must be confessed that as yet no absolutely trustworthy method for complete analysis has been found. The composition of most of the salts prepared in this investigation was deduced from the determinations of water of crystallisation and lead. The water was determined by heating to 110° for three hours a portion of the salt thoroughly dried by pressing between drying paper. In another portion the lead was determined thus: A weighed portion of the salt (about 1 gram) was introduced into an Erlenmeyer flask of 125 cc. capacity. Sulphuric acid sufficient to decompose the salt was introduced into the flask, which was then inclined in order to prevent loss, and gentle heat applied until all the iodine was driven off. The lead and potassium were then in the form of sulphates. A close examination of the flask showed that small yellow particles of lead iodide remained undecomposed on the sides of the flask. These were washed down with concentrated sulphuric acid, and the mass thoroughly boiled for about an hour longer in order to insure the conversion of all the lead into sulphate. After cooling, the mass was diluted with water to about 100 cc. and a small quantity of alcohol added. The whole was then allowed to stand until the supernatant liquid became perfectly clear, when it was filtered through a Gooch crucible. The lead sulphate was then washed thoroughly, first with water to which a little sulphuric acid and alcohol had been added, in order to remove all traces of potassium sulphate, then with water containing a little alcohol in order to remove all sulphuric acid. The crucible was then dried thoroughly at 110° and finally heated to a low red heat, allowed to cool in a desiccator for twenty minutes and weighed. To determine the potassium by simple evaporation of the filtrate containing potassium sulphate and sulphuric acid is not practicable on account of the large excess of sulphuric acid necessarily present. Experiments were made on the separation of lead as sulphide by hydrogen sulphide, but it was found that in every case some of the lead sulphide remained in solution, in consequence of the presence of the alkali halide. Various other methods were tried, all of which proved of no value.

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[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1890.

[2] Ann. chim. phys. [2] **34**, 366. [3] Ibid. [5] **24**, 226. [4] Ibid. [5] **29**, 289.

The method finally adopted for complete analysis is as follows:

1. In one portion of the salt, water of crystallisation was determined by heating in an air-bath for three hours at 110°.

2. In a second portion, lead was determined by conversion into the sulphate, as described above.

3. In a third portion, iodine and potassium were determined

thus: about 1 gram of the salt was treated with 100 cc. water in a small beaker. This was stirred thoroughly in order to insure complete decomposition of the salt, and filtered through a Gooch crucible *without washing*, for if water be added to the filtrate lead iodide separates. The iodine in the filtrate was then precipitated as silver iodide. The residue on the Gooch crucible was then washed with cold water, and the washings again passed through the crucible in order to retain any lead iodide which may have separated, and to insure all potassium iodide being removed from the crucible. This second filtrate was then added to the first, in which silver nitrate was present in excess. The silver iodide was then washed, dried and weighed. The lead iodide on the crucible was then dried and weighed. From the combined results of lead iodide and silver iodide the total amount of iodine was calculated.

4. The filtrate from the silver iodide was then treated with hydrogen sulphide in order to remove all lead and silver, filtered and evaporated to dryness with a little sulphuric acid. The residue of potassium sulphate was then heated to redness, allowed to cool, and weighed. From this the weight of potassium was calculated.

An analysis of one of the specimens obtained gave the following results:

I. 1.2486 grams salt lost 0.0683 gram H_2O.

II. 0.8166 gram salt gave 0.3687 gram $PbSO_4 = 0.2518$ gram Pb.

III. 1.4549 grams salt gave 0.9057 gram $PbI_2 = 0.4989$ gram I, and 0.622 gram $AgI = 0.3361$ gram I. (Total $I = 0.8350$ gram.)

IV. 1.4549 grams salt gave 0.2018 gram $K_2SO_4 = 0.0906$ gram K.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.84
I	57.43	57.39
K	5.91	6.23
H_2O	5.43	5.47

This salt was evidently the salt $KPbI_3.2H_2O$. As this analysis showed that the methods for determining water of crystallisation and lead were reliable, all the salts were identified by the determinations of these constituents. In all the calculations the atomic weights given by Meyer and Seubert were used.

Potassium Iodoplumbite.

I. *Salt of the composition* $KPbI_3.2H_2O$ ($PbI_2.KI.2H_2O$). The first work on the subject of the combinations of lead iodide with potassium iodide was done by Boullay,[1] who in 1827 announced, as the result of his work, the existence of the two salts $PbI_2.KI$ ($KPbI_3$) and $PbI_2.4KI$ (K_4PbI_6). The latter forms a very marked exception to the law of combination of the alkali halides with other halides. As the work of Boullay had been carried out quite a long time ago it was deemed advisable to repeat it, for at that time quantitative determinations were not so accurate as at present, and, furthermore, the filter-pump had not then been invented, so that the method of preparation of the salts must have been rather crude. The first efforts were therefore directed to the preparation of the salt $PbI_2.KI$ ($KPbI_3$) described by Boullay. The potassium iodide used in these experiments was purified by decomposing any iodate present by zinc amalgam.[2] The lead iodide first used was prepared by precipitating a solution of pure lead nitrate with pure potassium iodide solution. Towards the latter part of the investigation commercial lead iodide was used. This gave results agreeing very closely with those obtained by using the lead iodide prepared for the purpose.

According to Boullay, when a solution of lead nitrate is added to a slightly concentrated solution of potassium iodide there is formed at first a red precipitate of lead iodide which soon turns white, owing to the conversion of the lead iodide into the double salt $PbI_2.KI$($KPbI_3$). Great trouble was experienced at first in preparing this salt. Boullay directed to use a solution of potassium iodide only slightly concentrated. In each of the preliminary experiments lead iodide was precipitated when a solution of lead nitrate was added to a solution of potassium iodide only slightly concentrated; but, on standing, whether cold or hot, there was no change to a white color as described by Boullay. But when a solution of potassium iodide slightly more concentrated was used and heat applied, it was noticed that yellow needles formed along the upper portion of the beaker in which the experiment was being conducted, where drops of the solution had spattered, these drops becoming more concentrated by evaporation. This observation suggested that if a more concentrated solution of potassium iodide were used the salt might be obtained. Experiments were then made to determine the exact conditions under which the salt is formed. Solutions of lead nitrate and of potassium iodide were prepared, each containing .25 gram of salt in 1 cc. Five portions of the lead nitrate solution of 5 cc. each were then measured out. To these were added quantities of potassium iodide solution (warm) varying from 5 cc. to 25 cc. Lead iodide was precipitated in each case, but on cooling the mass did not in any case turn white, as described by Boullay. So to five portions more (5 cc. each) of the potassium iodide solution were added successively quantities of solid potassium iodide varying from 0.25 gram to 1.25 grams. These portions were heated and added to 5 cc. portions of the lead nitrate solution. Lead iodide was precipitated in each case, but still there was no double salt formed; so, again to five portions (5 cc. each) of the potassium iodide solution were added quantities of solid potassium iodide varying from 3 grams to 5 grams. The solutions were then heated and added to five portions (5 cc. each) of the lead nitrate solution. Lead iodide was precipitated in each case, but gradually the red precipitate became white, the most concentrated solution becoming white first. On heating, the white salt was decomposed and insoluble lead iodide remained, having the form of the original crystals; but, on cooling, the crystals again became white, owing to the formation of the double salt, as described by Boullay. This slightly yellowish salt was freed from the mother-liquor as much as possible by means of a filter-pump, then pressed between drying paper and placed in a desiccator for twelve hours. The analysis gave the following results:

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[1] Ann. chim. phys. [2] **34**, 366.

[2] This Journal **10**, 321.

I. 0.9779 gram salt lost 0.0111 gram H_2O.

II. 1.6154 grams salt gave 0.7023 gram $PbSO_4$ = 0.4797 gram Pb.

III. 1.0204 grams salt, after standing over sulphuric acid one week, lost 0.0028 gram.

	Calculated for $KPbI_3$ ($PbI_2.KI$).		Found.	
		I.	II.	III.
Pb	33.02	...	29.70	...
H_2O	...	1.14	...	0.273

Plainly this salt lost its water of crystallisation by standing over sulphuric acid. From the mother-liquor of this salt there crystallised after twelve hours long needles of slightly yellowish tint. By a slight elevation of temperature these needles are redissolved in the mother-liquor, but by rapidly heating the beaker containing the mass the needles are decomposed, lead iodide remaining, which retains the form of the original crystals. On cooling these needles again became white. The explanation of the formation of these long needles in the mother-liquor will be given under the head of the salt $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$).

The salt $KPbI_3$ ($PbI_2.KI$) was then prepared in larger quantities by using the following proportions: 4 grams of lead nitrate were dissolved in 15 cc. of water, and 15 grams potassium iodide in 15 cc. of water. The latter solution was then heated and added to the nitrate solution, which was stirred and kept cold. The double salt thus formed was pumped dry and thoroughly pressed between drying paper. The analysis of this salt gave the following results:

I. 1.3640 grams salt lost 0.0712 gram H_2O.

II. 1.1614 grams salt lost 0.0610 gram H_2O.

III. 1.0744 grams salt gave 0.4842 gram $PbSO_4 = 0.3307$ gram Pb.

IV. 1.3640 grams salt gave 0.6162 gram $PbSO_4 = 0.4209$ gram Pb.

V. 0.8867 gram salt gave 0.4002 gram $PbSO_4 = 0.2733$ gram Pb.

	Calculated for $KPbI_3.2H_2O$.			Found.		
		I.	II.	III.	IV.	V.
Pb	31.23	...	...	30.78	30.86	30.82
H_2O	5.43	5.22	5.25	...	...	...

This was evidently the salt $KPbI_3.2H_2O$. Boullay prepared this salt, but dried it over lime; accordingly he found only 3 per cent. H_2O, and says:[1] "Si l'on suppose que, dans ce sel, les deux iodures soient à l'état d'hydriodates, il foudrait 4.16 l'eau pour 100 parties du sel humide; je n'en ai trouvé que 3.00."

In speaking of the formation of this salt, Boullay states that it is always formed when a slightly concentrated solution of potassium iodide is brought together, hot or cold, with an *excess of lead iodide*. It is difficult to understand why he should have made this statement, as it is evident from his work on the subject that he never worked with an excess of lead iodide, but that in each case lead iodide was first precipitated, and this was then converted into the double salt, or rather iodoplumbite, by the excess of potassium iodide in the solution. However, in order to test his statement strictly, a solution of potassium iodide not quite saturated at 20° was added to a large excess of lead iodide in a beaker, and stirred thoroughly. On first cooling, the excess of lead iodide collected at the bottom of the vessel, while the supernatant liquid remained clear; but on the following day silky, needle-shaped crystals were found in the solution and also mixed with unchanged lead iodide in the bottom of the vessel. The best crystals were removed from the solution, dried and analysed, giving the following results:

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[1] Ann. chim. phys. [2], **34**, 367.

0.2150 gram salt gave 0.0957 gram $PbSO_4 = 0.0654$ gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.42

This was therefore the same salt as has been previously prepared.

Some of the needle-shaped crystals of the salt $KPbI_3.2H_2O$ were then heated to 140° to test whether any more water could be driven off than at 110°, but no further loss of weight was found. The further effect of heat upon this salt was tried in this way. Some of the needle-shaped crystals were placed in an ignition tube; this in turn was placed in a sulphuric acid bath and the temperature raised gradually. At 70° water began to be given off, the salt becoming a brighter yellow and decreasing considerably in bulk. As the temperature was raised the amount of water given off increased to such an extent that it collected in large drops on the side of the tube. These drops falling on the salt below decomposed it instantly, as was shown by the color of the lead iodide which appeared. Thus the same water which had been present in the compound as water of crystallisation, after having been once driven out by heat, served to decompose the anhydrous salt when brought in contact with it. By using an ignition tube, bent at an angle in order to prevent the water falling back upon the salt, it was found that at about 310° the salt decomposed, iodine being given off. Treated with absolute alcohol, this salt is decomposed just as when treated with water.

II. *Salt of the composition* K_4PbI_6 ($PbI_2.4KI$). — While attempting to determine the concentration at which the salt $KPbI_3.2H_2O$ was formed, as mentioned above, efforts were made to prepare the salt K_4PbI_6 ($PbI_2.4KI$) described by Boullay[1] under the head of "Bibasic iodoplumbate of iodide of potassium." He obtained it by adding lead iodide to a concentrated solution of potassium iodide, this last being in excess. He represented the composition of the salt by the formula "$2KaI_4 + PbI_4$," or, according to the present atomic weights, $PbI_2 + 4KI$. This formula was based upon the following analyses:

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[1] Ann. chim. phys. [2] **34,** 370.

	Found.		Calculated for
	I.	II.	$PbI_2 + 4KI$.
PbI_2	34.0	36.0	41.0
KI	66.0	64.0	59.0

To a cold saturated solution of potassium iodide lead nitrate was added, and a yellowish white salt was obtained. This was the first compound of lead and potassium iodides obtained during the course of the investigation, and was dried not by pumping off the mother-liquor, but by simple filtration, then pressing between drying paper for a short time, and finally completely dried by standing over lime, the method adopted by Boullay.

On analysis this salt showed:

I. 1.2961 grams salt lost 0.0388 gram H_2O.

II. 1.2734 grams salt lost 0.0191 gram H_2O.

III. 0.3880 gram salt gave 0.1435 gram $PbSO_4 = 0.0980$ gram Pb.

IV. 2.3640 grams salt gave 0.9015 gram $PbSO_4 = 0.6157$ gram Pb.

	Calculated for			Found.	
	$PbI_2.4KI$.	I.	II.	III.	IV.
Pb	18.40	...	...	25.26	26.04
H_2O	...	2.99	1.50	...	...

These results plainly show that the salt K_4PbI_6 ($PbI_2.4KI$) had not been obtained, but rather a salt approaching in composition the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) described by Ditte,[1] with the exception of the water, which showed by the difference in the two analyses, the second having been made several days after the first, that water was abstracted by the lime over which the salt stood. The preparation of this salt and its analyses were rather crude, as they were the first attempts; however, the results were sufficient to show that the salt K_4PbI_6 ($PbI_2.4KI$) had not been obtained under the conditions described by Boullay. Later in the investigation, after skill in dealing with these compounds had been acquired, another attempt was made to prepare the salt, following the directions of Boullay, with the exception that the salt, instead of being dried over lime, was pressed for several days between drying paper. On analysis this salt showed:

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[1] Ann. chim. phys. [5] 24, 226.

I. 1.2106 grams salt lost 0.0634 gram H_2O.

II. 0.9371 gram salt lost 0.0490 gram H_2O.

III. 1.0085 grams salt gave 0.4569 gram $PbSO_4 = 0.3121$ gram Pb.

IV. 0.8693 gram salt gave 0.3914 gram $PbSO_4 = 0.2673$ gram Pb.

	Calculated for		Found.			
	K_4PbI_6.	$KPbI_3.2H_2O$.	I.	II.	III.	IV.
Pb	18.40	31.23	...	...	30.95	30.75
H_2O	...	5.43	5.24	5.23	...	...

The salt was evidently the salt $KPbI_3.2H_2O$. These last results differ very widely from those first obtained in trying to prepare the salt K_4PbI_6; in the first case the percentage of lead is 25.26, in the second case 30.95. Many efforts were then made to obtain the salt which showed 25.26 per cent. of lead, varying the conditions in all possible ways, but in no case was a salt obtained even approaching this composition. Therefore it seems justifiable to conclude that the salt yielding 25.26 per cent. of lead which was prepared and analysed in a rather rough way, must have been very impure, owing to excess of potassium iodide present. From the above facts it appears to follow that the salt K_4PbI_6 ($PbI_2.4KI$) does not exist, and that the mass which Boullay considered to have this composition was a mixture of the salt $KPbI_3.2H_2O$ with a large excess of potassium iodide.

III. *Salts of the composition* $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) and $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$).—Since the paper published by Boullay in 1827, the principal work on the double iodides of lead and potassium has been done by Ditte, and also by Berthelot. Ditte[1] described the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$), giving an account of its method of formation, appearance and general behavior, and studied its decomposition by water.

Berthelot[2] then took up the subject and described the two salts, $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$) and $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$). This investigation was now directed to the repetition of the work of these chemists. Both agree that the salt containing lead and potassium iodides, in the proportion of one part of lead iodide to two parts of potassium iodide, is formed whenever lead iodide is added to a warm solution of potassium iodide and the solution allowed to cool. Ditte states that the salt is formed also in the cold.

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[1] Ann. chim. phys. [5] **24**, 226.

[2] Ann. chim. phys. [5], **29**, 289.

As previously stated, when this investigation was first begun a salt was obtained which seemed to have the composition $K_2PbI_4 + H_2O$ ($PbI_2.2KI + H_2O$), the water of crystallisation not being constant. But now, on the first attempt to repeat the work of Ditte, a salt was obtained resembling in appearance that described by him, but on analysis it gave the following results:

I. 1.2227 grams salt lost 0.0413 gram H_2O.

II. 2.1526 grams salt gave 0.9541 gram $PbSO_4 = 0.6517$ gram Pb.

III. 0.9733 gram salt gave 0.4296 gram $PbSO_4 = 0.2934$ gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.4H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	23.93	31.23	...	30.28	30.14
H_2O	8.33	5.43	3.38	...	...

Evidently this salt agreed more closely with the formula $KPbI_3.2H_2O$ than $K_2PbI_4.4H_2O$. The water of crystallisation varied in this salt, as it was dried over lime, as was the case with several of the preceding salts. The salt just mentioned was prepared from a hot solution. As it had been shown earlier that heat decomposed the salt $KPbI_3.2H_2O$ with separation of lead iodide, it was thought probable that the salt $K_2PbI_4.4H_2O$ might be prepared in the cold. To this end 15 cc. of a cold saturated solution of potassium iodide was added to 10 cc. of a cold saturated solution of lead nitrate. The lead iodide first precipitated soon turned white, owing to the formation of the double salt. The mass having become quite pasty, more of the potassium iodide solution was added, enough to render the mass quite mobile and to insure the conversion of all lead iodide into the double salt. The salt prepared in this way was analysed by boiling with sodium carbonate, the lead iodide being thus changed to the carbonate. This was then filtered through a Gooch crucible, washed thoroughly and ignited at a low red heat. The lead was then weighed as oxide. Analysed in this way the following results were obtained:

I. 1.7823 grams salt lost 0.0966 gram H_2O.

II. 1.6530 grams salt lost 0.0892 gram H_2O.

III. 1.7823 grams salt gave 0.5990 gram $PbO = 0.5560$ gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.4H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	23.93	31.23	...	...	31.20
H_2O	8.33	5.43	5.42	5.39	...

As the effort to prepare the salt $K_2PbI_4.4H_2O$ in the cold had failed, it was then attempted to prepare it by heating a cold saturated solution of potassium iodide almost to boiling, then adding lead iodide to saturation; but this was found impracticable, since such large quantities of lead iodide are taken up by the solution that the double salt begins to separate from the solution at the surface while lead iodide is still being dissolved. So to a hot solution of potassium iodide (cold saturated) lead iodide was added in large quantities, but not enough to cause the separation of the double salt, as mentioned above. On cooling, pale yellow needles separated. These were dried and marked No. 1. The filtrate from this salt was moderately diluted with water, and soon light-colored needle-shaped crystals were seen to appear. On standing for a short time the whole mass became almost solid, owing to the thick network of crystals formed. These were dried and marked No. 2. By continuing the dilution crystals again began to appear, but now on adding more water these crystals were decomposed into lead iodide and potassium iodide. However, on stirring the mass thoroughly the original white color was restored. These crystals were dried and marked No. 3. By further dilution of the filtrate still another crop of crystals were obtained. These were dried and marked No. 4. On adding water to a small portion of the filtrate, decomposition took place immediately, lead iodide separating in large quantities. But on treating another portion of the filtrate with alcohol a flocculent white salt separated, which on close examination seemed to be composed of little needles. These were dried and marked No. 5. It was thought that these five salts would prove to be a series of compounds showing a gradation in composition. On analysis these salts gave the following results:

I. 1.5388 grams of salt No. 1 lost 0.0813 gram H_2O, and 1.6216 grams of salt No. 1 gave 0.7300 gram $PbSO_4 = 0.4986$ gram Pb.

II. 1.2032 grams salt No. 2 lost 0.0617 gram H_2O, and 1.1969 grams salt No. 2 gave 0.5391 gram $PbSO_4 = 0.3682$ gram Pb.

III. 1.2780 grams salt No. 3 lost 0.0673 gram H_2O and gave 0.5782 gram $PbSO_4 = 0.3949$ gram Pb.

IV. 1.1226 grams salt No. 4 lost 0.0590 gram H_2O and gave 0.5096 gram $PbSO_4 = 0.3481$ gram Pb.

V. 1.2413 grams salt No. 5 lost 0.0639 gram H_2O and gave 0.5637 gram $PbSO_4 = 0.3850$ gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	II.	III.	IV.	V.
Pb	31.23	30.75	30.76	30.90	31.01	31.02
H_2O	5.43	5.28	5.13	5.27	5.26	5.15

The results here, as in almost all of the analyses, are below the theoretical. This is to be expected, as the mother-liquor, which is rich in potassium iodide, cannot be washed from the salts, but has to be removed by pressing between drying paper. This would plainly lead to low results for water and lead, and at the same time high results for iodine and potassium.

An examination of the above results shows that instead of obtaining a series of salts the same salt was obtained in every case, becoming gradually purer as the solution was diluted. Boullay observed this same phenomenon. These facts also show that the same salt, $KPbI_3.2H_2O$, is obtained, and not the salt $K_2PbI_4.4H_2O$, described by Ditte, whether a hot concentrated or a cold solution of potassium iodide be used, decreasing from considerable concentration to just above the point where separation of lead iodide takes place; and still further, alcohol separates the same salt from this last most dilute solution. This is very strong evidence against the existence of the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$), described by Ditte, or $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$), described by Berthelot.

Another solution was then prepared similar to that from which the salt marked No. 1 had been obtained, but instead of filtering from the crystals formed, water was added. Lead iodide at first separated, but by stirring the mass thoroughly the original color was restored. In this way a large quantity of water was added, until finally, by further addition of water to a small portion of the mass, lead iodide was seen to separate, and remained undissolved even after thorough stirring. The analysis of the salt thus formed proved it to be the salt $KPbI_3.2H_2O$.

Efforts were then made to prepare the salt $K_2PbI_4.4H_2O$ by dissolving the salt $KPbI_3.2H_2O$ in a large excess of a cold saturated solution of potassium iodide. On heating, the salt dissolved, and on cooling, long needle-shaped crystals separated, similar in appearance to the salt which had been dissolved. On analysis this salt gave the following results:

I. 1.0974 grams salt gave 0.4942 gram $PbSO_4 = 0.3375$ gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.75

On following the directions of Ditte[1] in every detail a salt was prepared which, when heated before being separated from its mother-liquor, decomposed. The lead iodide so formed retained the form of the original crystals. On filtering now and allowing to cool, a network of needle-shaped crystals was obtained which almost completely filled the solution. On analysis this salt gave the following results:

I. 1.2172 grams salt lost 0.0650 gram H_2O.

II. 0.8487 gram salt gave 0.3836 gram $PbSO_4 = 0.2620$ gram Pb.

	Calculated for		Found.	
	$KPbI_3.2H_2O$.	$K_2PbI_4.4H_2O$.	I.	II.
Pb	31.23	23.93	...	30.87
H_2O	5.43	8.33	5.34	...

This was evidently the same salt which had been obtained in all the previous experiments.

Ditte[2] describes another method for the preparation of the salt $K_2PbI_4.4H_2O$. As all previous efforts to prepare the salt had failed, it was thought that possibly by this means the salt might be obtained, or, on the other hand, conclusive evidence obtained that the salt does not exist.

This method of preparation consists in mixing freshly precipitated lead carbonate with an excess of a cold saturated solution of potassium iodide. No action takes place at ordinary temperatures, but on passing a current of carbon dioxide through the mixture for about twenty minutes the white lead carbonate is replaced by the yellowish crystals of the double salt. A salt prepared in this way gave on analysis the following results:

I. 0.9316 gram salt lost 0.0492 gram H_2O.

II. 1.0653 grams salt gave 0.4908 gram $PbSO_4 = 0.3352$ gram Pb.

III. 0.8595 gram salt gave 0.3958 gram $PbSO_4 = 0.2703$ gram Pb.

	Calculated for		Found.	
	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	31.23	...	31.47	31.45
H_2O	5.43	5.28	...	...

It is clear that this method for the preparation of the salt $K_2PbI_4.4H_2O$ also failed.

The salt $K_2PbI_4.2H_2O$ described by Berthelot[3] was obtained, to use his own words, "par le froidissement de la solution de l'iodure de plomb dans une solution concentrée d'iodure de potassium." Plainly this condition has been tried repeatedly in the effort to prepare the salt $K_2PbI_4.4H_2O$ (Ditte), but in order to be absolutely certain that this salt of Berthelot could not be prepared, three successive attempts were made, varying the conditions slightly in each case. The salts obtained in this way gave on analysis the following results:

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[1] Ann. chim. phys. [5] **24**, 226.
[2] Ibid. [5] **24**, 235.
[3] Ibid. [5] **29**, 289.

I. 1.0975 grams salt No. 1 lost 0.0565 gram H_2O, and 1.3778 grams salt No. 1 gave 0.6141 gram $PbSO_4 = 0.4194$ gram Pb.

II. 1.3876 grams salt No. 2 lost 0.0724 gram H_2O, and 0.6197 gram salt No. 2 gave 0.2738 gram $PbSO_4 = 0.1870$ gram Pb.

III. 0.9158 gram salt No. 3 lost 0.0477 gram H_2O, and 0.8046 gram salt No. 3 gave 0.3569 gram $PbSO_4 = 0.2438$ gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.2H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	24.97	31.23	30.44	30.18	30.30
H_2O	4.35	5.43	5.15	5.22	5.21

The results show that all three salts have the composition $KPbI_3.2H_2O$. Solutions of potassium iodide saturated at 100° were then used, but were soon found to be of no value, as, when a rather small quantity of lead iodide was added, on cooling, a large mass of potassium iodide crystallised out along with the double salt; and when a large quantity of lead iodide was added the mass soon became unmanageable, on account of the large amount of double salt present in the solution, so that it could not be filtered or purified in any way.

From all of the above facts it is to be concluded that the salts $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) and $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$) cannot be made; for not only have the directions of both Ditte and Berthelot been closely followed, but, furthermore, the conditions have been changed, using at one time hot solutions, at another cold, at one time cold saturated, at another dilute; again a solution of potassium iodide saturated at 100° was employed, and in every case the salt $KPbI_3.2H_2O$ was obtained. Further, the attempt was made to obtain the salt by dissolving the salt $KPbI_3.2H_2O$ in a cold saturated solution of potassium iodide, and finally by passing carbon dioxide through a mixture of lead carbonate and potassium iodide solution, and here likewise was obtained the salt $KPbI_3.2H_2O$.

IV. *Salt of the composition* $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$).— This salt was described by Berthelot.[1] He in turn ascribes it to Boullay, but gives no reference to any article by Boullay. Accordingly, careful search was made for Boullay's description of this salt while looking for his account of the salt K_5PbI_7 ($PbI_2.5KI$), mentioned above, but this search was unsuccessful.

Berthelot states that it is formed by slow cooling of the mother-liquor from the salt $K_2PbI_4.2H_2O$, which, in turn, is prepared by adding lead iodide to a concentrated solution of potassium iodide. These directions were closely followed. The mother-liquor from the salt which first separated on cooling was surrounded by water in order to lower the temperature, and was then allowed to stand four days. Long, yellow needles separated which on analysis gave the following results:

I. 0.7839 gram salt lost 0.0382 gram H_2O.

II. 0.9913 gram salt gave 0.4012 gram $PbSO_4$ = 0.2740 gram Pb.

	Calculated for		Found.	
	$K_4Pb_3I_{10}.6H_2O$.	$K_3Pb_2I_9.4H_2O$.	I.	II.
Pb	28.82	27.75	...	27.64
H_2O	5.02	4.83	4.87	...

This analysis seemed to show that the salt had the composition $K_3Pb_2I_9.4H_2O$ ($2PbI_2.3KI.4H_2O$). In order to confirm this the experiment was repeated. The mother-liquor in this case was surrounded by ice. Long needles crystallised from the solution, but in addition, considerable quantities of potassium iodide also separated. So the whole was heated gently until all had passed into solution, and then allowed to cool. The following night was very cold, and on examining the beaker the next morning there could be seen both the double salt and potassium iodide. This was heated again until all dissolved, and after several trials at different temperatures, finally a good crop of long needle-shaped crystals was obtained which were apparently free from potassium iodide. This salt on analysis showed:

I. 1.2129 grams lost 0.0647 gram H_2O.

II. 0.6945 gram salt gave 0.3140 gram $PbSO_4$ = 0.2145 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.	
		I.	II.
Pb	31.23	...	30.88
H_2O	5.43	5.33	...

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[1] Ann. chim. phys. [5] **29**, 289.

These results showed that most probably in the first preparation of the salt the temperature was reduced too low, so that the salt was mixed with potassium iodide. In order to test this view and confirm the last experiment the work was very carefully repeated, accurate measurements being made at each stage, as follows: 100 cc. of a solution (saturated at 22°) was heated. When the temperature reached 75° lead iodide was added gradually while the temperature was being raised to 100°. In this way 17.5084 grams were added. The solution was then allowed to cool. At 34° needle-shaped crystals began to separate. The cooling was continued until the temperature reached 22°. The mother-liquor was then pumped off and placed under a bell-jar, where it was allowed to stand three days, the temperature varying only slightly above or below 18°. Long, needle-shaped crystals separated as before, and apparently free from potassium iodide. On analysis this salt showed:

I. 0.9263 gram salt lost 0.0474 gram H_2O.

II. 1.2400 grams salt gave 0.5548 gram $PbSO_4 = 0.3789$ gram Pb.

	Calculated for		Found.	
	$K_4Pb_3I_{10}.6H_2O$.	$KPbI_3.2H_2O$.	I.	II.
Pb	28.82	31.23	...	30.56
H_2O	5.02	5.43	5.12	...

From these facts it seems probable that the salt described by Berthelot as $3PbI_2.4KI.6H_2O$ ($K_4Pb_3I_{10}.6H_2O$) was really a mixture of the salts $KPbI_3.2H_2O$ and potassium iodide. Indeed this is rendered almost certain when it is remembered that at the temperature and concentration used the potassium iodide, which is present in the solution in large excess, separates very easily, as has already been shown.

Sodium Iodoplumbite, $NaPbI_3$.

The literature on this subject is very limited. Boullay[1] states that it is probable that the other alkali iodides would act like potassium iodide in regard to the formation of the double halide, but makes no experiments on the subject. Ditte[2] dismisses the subject by stating that sodium iodide behaves like potassium iodide, but gives no experimental data. Poggiale[3] mentions a double iodide of lead and sodium, to which he ascribes the formula $PbI_2.NaI$ ($NaPbI_3$). Efforts were first made to obtain this salt. For this purpose 100 grams of sodium iodide were dissolved in 75 cc. water at 20°. Lead iodide was then added until no more would dissolve, about 60 grams being thus added. This solution, on standing, deposited no crystals. The double salt is therefore much more soluble than the corresponding potassium salt. The solution was then heated and 10 grams more of lead iodide added. On cooling, nothing crystallised out, so the solution was then evaporated to about two-thirds of its former volume. On cooling, small needle-shaped crystals separated, closely resembling in appearance the potassium salt. These crystals formed in such large quantities that the mass almost completely solidified. Like the potassium salt this salt is decomposed by water and also by heat with separation of lead iodide. Great difficulty was experienced in purifying this salt, for such large quantities of sodium iodide were mixed with it. Various methods for purification were tried; for example, as sodium iodide is very deliquescent, it was hoped that by allowing the mixture to stand exposed to moist air, enough water would be taken up to dissolve the sodium iodide and leave the double salt behind, but this proved unsuccessful. The method finally adopted was as follows: The mixture was exposed to the air until a considerable quantity of water had been absorbed. The undissolved portion, on being pressed with a stirring rod, was found to contain hard granular crystals of sodium iodide. Gentle heat was then applied, and it was soon found that the granular crystals had disappeared, a bright yellow salt remaining. The heating was now discontinued and the mass filtered rapidly by means of a filter-pump (for if the heating be continued the whole passes into solution). The salt was then pressed between drying paper for several days, and at the end of that time was found still to be moist, showing that the salt itself is deliquescent. It was then dried in an air-bath at 110°. The anhydrous salt, which is reddish yellow, gave on analysis the following results:

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[1] Ann. chim. phys. [2] **34**, 372.

[2] Compt. rend. **92**, 1343.

[3] J. prakt. Chem. **35**, 329.

I. 0.8511 gram salt gave 0.4326 gram $PbSO_4 = 0.2955$ gram Pb.

	Calculated for $NaPbI_3$.	Found.
Pb	33.89	34.71

The composition of the salt is therefore very probably $NaPbI_3$. Nothing definite can be said in regard to the water of crystallisation, as the salt is so deliquescent that it cannot be obtained dry at ordinary temperatures.

Potassium Bromoplumbite, $KPbBr_3.H_2O$.

The only work on this subject up to the present time is that done by Berthelot.[1] This was very unsatisfactory, however, and indeed he remarks that the substances obtained by him are not to be regarded as true chemical compounds, but as mixtures of the double salt with potassium bromide or lead bromide. He gives, however, the composition of one salt obtained as $3PbBr_2.2KBr$. Efforts were made to determine whether a definite compound of lead and potassium bromides could be obtained. It was found that if to a solution of potassium bromide (saturated at 20°) a solution of lead nitrate (saturated at 20°) be added drop by drop, the lead bromide so formed was dissolved on constant stirring until quite a large quantity had been dissolved, though not nearly so large a quantity as in the case of the iodides. When all the lead bromide possible had been dissolved the solution was allowed to stand, and in a few hours colorless crystals began to appear. After several days these tabular crystals grew to considerable size. The finely powdered salt gave on analysis the following results:

I. 0.7823 gram salt lost 0.0276 gram H_2O.

II. 1.1592 grams salt lost 0.0404 gram H_2O.

III. 1.2551 grams salt gave 0.7497 gram $PbSO_4$=0.5120 gram Pb.

IV. 0.9297 gram salt gave 0.5570 gram $PbSO_4$=0.3804 gram Pb.

	Calculated for $KPbBr_3.H_2O$.	Found.			
		I.	II.	III.	IV.
Pb	41.06	...	...	40.80	40.92
H_2O	3.57	3.53	3.49	...	...

This salt was repeatedly prepared afterwards and the analyses leave no doubt that the composition is $KPbBr_3.H_2O$. The form of the crystals was the same in every case.

Similar efforts were made to prepare the corresponding sodium bromoplumbite, but without success. It was thought at one time that the salt had been obtained, as lath-shaped crystals separated from the solution of lead bromide in sodium bromide. This salt, however, proved on analysis to be lead bromide. Efforts were also made to prepare the salt by using a hot sodium bromide solution, but the salt which separated on cooling proved to be lead bromide. The salt appears to be formed in solution, but as yet it has been found impossible to isolate it.

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[1] Ann. chim. phys. [5] **29**, 293.

Potassium Chloroplumbite, $KPbCl_3$.

The statements made by Berthelot[1] in regard to this salt are as indefinite as those which he makes in regard to the bromoplumbite. Strohecker[2] also mentions the existence of double salts of lead and potassium chlorides, but gives no formulas.

The investigation was turned to the preparation of this salt, potassium chloroplumbite. A cold saturated solution of potassium chloride was heated to boiling and a solution of lead nitrate (cold saturated) added drop by drop, the mass being continually stirred. Lead chloride was dissolved, but not so much of the lead salt as in the case of the iodide and bromide. On cooling, a salt crystallised out in fine white needles, which on analysis gave the following results:

I. 1.2142 grams salt gave 1.0281 grams $PbSO_4$=0.7022 gram Pb.

II. 1.2039 grams salt gave 1.0176 grams $PbSO_4$=0.6950 gram Pb.

	Calculated for $KPbCl_3$.	Found.	
		I.	II.
Pb	58.71	57.81	57.73

There is no water of crystallisation in this salt. If the solution be cooled slowly and kept at about 35° the potassium chloroplumbite can be obtained in lenticular crystals, somewhat needle-shaped. These crystals have the same composition as the salt already mentioned above, but they contain some water mechanically held in the crystals, for on heating to about 200° the salt decrepitates just as potassium chloride does when heated. This salt is necessarily impure on account of the large excess of potassium chloride present in the solution.

All efforts to prepare the sodium chloroplumbite failed. A salt crystallising in radiating leaflets was obtained, but this by analysis was proved to be lead chloride.

The work on the fluorplumbites could not be carried to any extent on account of lack of time, but a few qualitative experiments showed that if a cold saturated solution of lead nitrate be added to a cold saturated solution of potassium fluoride, heated almost to boiling, a small portion of the lead fluoride so formed is dissolved. Less of the lead salt is dissolved in this case, however, than in the case of either the iodide, bromide, or chloride.

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[1] Ann. chim. phys. [5] **29**, 293.

[2] Jahresbericht, 1869, 282.

It was hoped that the investigation could be extended to the mixed halides, but want of time prevented this.

Conclusion.

The principal results of this investigation may be summed up as follows:

I. Of the five iodoplumbites of potassium described by Boullay, Ditte and Berthelot, only one exists. This is the salt $KPbI_3.2H_2O$.

II. The bromoplumbite of potassium is a well crystallised compound, having the composition $KPbBr_3.H_2O$.

III. The chloroplumbite of potassium can also be prepared in well formed crystals, and has the composition $KPbCl_3$.

IV. The quantity of the lead halide dissolved in the alkaline halide increases with the atomic weight of the halogen. Only a small quantity of lead fluoride dissolves in a solution of potassium fluoride, a larger quantity of lead chloride in potassium chloride solution, a still larger quantity of lead bromide in potassium bromide solution, and greatest of all, lead iodide in potassium iodide solution.

V. The corresponding sodium salts, if formed, are separated with great difficulty, as in the case of the iodoplumbite, while no salt was isolated in the case of the sodium bromo or chloroplumbite.

VI. All these salts are decomposed by water, and in order that they may exist in solution a certain minimum amount of alkali halide must be present, this amount varying inversely as the atomic weight of the halogen atom present in the compound.

VII. The amount of the water of crystallisation decreases with the atomic weight of the halogens, thus: $KPbI_3.2H_2O$, $KPbBr_3.H_2O$, and $KPbCl_3$.

VIII. Finally, it is seen that the composition of all these salts can be expressed by formulas in which two halogen atoms play the part of the so-called linking oxygen atom, thus proving these salts to be no exception to the law of combination of alkali halides with other halides put forward by Professor Remsen.

III.—ON SOME DOUBLE HALIDES OF MANGANESE.[1]

BY CHARLES E. SAUNDERS.

The following is a list of the salts hitherto described containing manganous chloride, combined with the chloride of some alkali metal (or of ammonium):

$NH_4MnCl_3.2H_2O$
$(NH_4)_2MnCl_4.H_2O$
$(NH_4)_2MnCl_4.2H_2O$
Rb_2MnCl_4
$Rb_2MnCl_4.3H_2O$
Cs_2MnCl_4
$Cs_2MnCl_4.3H_2O$
$2(Cs_2MnCl_4).5H_2O$.

Each of the salts in this very irregular series will be considered in detail in its proper connection. There is, however, a salt which should be considered before taking up the compounds in this list and those closely related to them.

Manganous Chloride, $MnCl_2.2H_2O$.

In attempting to prepare a double chloride of manganese and lithium, and also of manganese and magnesium, a substance was obtained which proved to be manganous chloride with two molecules of water of crystallisation instead of four, which is the normal number. The new form of the substance was obtained by adding a considerable quantity of ordinary manganous chloride to a concentrated solution of lithium chloride in water, then evaporating somewhat and allowing to cool. When magnesium chloride was used instead of lithium chloride, either alcohol containing water, or water alone served as the solvent, a few drops of hydrochloric acid being usually added. When magnesium chloride is present there must be added a considerable excess of manganous chloride, or a double salt will be produced instead of the simple chloride. Manganous chloride, as thus obtained, crystallised in beautiful pink crystals, usually about one centimeter in length and quite slender. The ends of the crystals were frequently hollow for some distance inward. They usually formed radiating groups, but were sometimes obtained in perfectly definite crossed twins. The substance acts in general like ordinary manganous chloride, except that, as would be expected, it does not lose water of crystallisation when dried over calcium chloride, while the ordinary form loses two of its four molecules under these conditions. Analysis showed that the same salt was obtained from a solution containing lithium chloride as from one containing magnesium chloride. From the conditions of formation a pure product could not, however, be expected. The analyses here given were made first with a sample which had been dried between filtering paper, and, second, with one dried to constant weight over calcium chloride.

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[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1891.

Analysis of salt dried between filtering paper gave the following results:

0.3924 gram salt gave 0.6753 gram AgCl (42.56 per cent. Cl), and 0.1788 gram Mn_3O_4 (32.82 per cent. Mn).

When dried over calcium chloride the salt gave the following figures on analysis:

0.3346 gram salt gave 0.5902 gram AgCl (43.62 per cent. Cl), and 0.1581 gram Mn_3O_4 (34.03 per cent. Mn).

0.2975 gram lost at 105°–110° 0.0326 gram $H_2O = 10.96$ per cent. H_2O.

At higher temperatures further, but slow, loss was observed, no doubt due to decomposition of the salt.

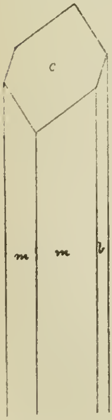

Fig. 1.

	Calculated for $MnCl_2.2H_2O$.		Found. In dried salt.	In undried salt.
Mn	54.80	33.94	34.03	32.82
2Cl	70.74	43.81	43.62	42.56
H_2O	17.96	11.125	10.96	
H_2O	17.96	11.125		
	161.46	100.000		

It is evident, therefore, that the salt has the formula $MnCl_2.2H_2O$, and loses one molecule of water at 105°.

Crystallography of the salt.—It crystallises in slender prisms (Fig. 1), which were shown by their optical properties and angular measurements to be monoclinic. The crystals were usually hollow towards the end, so that the basal plane was very imperfectly developed. On this account the crystallographic angle β was found (roughly) by measurement on a petrographical microscope, the crystal resting on one of the clinopinacoids. The other angle was measured on a Fuess goniometer. The forms observed were:

$c = 0P$, [001].
$m = \infty P$, [110].
$b = \infty P \grave{\infty}$, [010].

The angles measured were: $m : m = 100° 45'$, and $\angle \beta = 42°$ (nearly). From these data, taking $\bar{b}$ as unity, we have $\grave{a} = 1.238$ (nearly).

The substance sometimes forms crossed twins in which the basal plane is the twinning plane. An orthographic projection of such a twin is shown in Fig. 2.

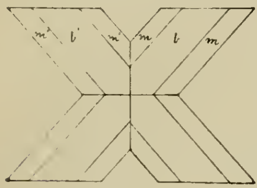

FIG. 2.

It seems probable that the magnesium chloride, or lithium chloride, present when manganous chloride crystallises out with only two molecules of water must act as a sort of dehydrating agent; and it is not unlikely that the presence of such salts as these in solutions in other cases would lead to the formation of crystals of various substances, containing less than their normal number of molecules of water.

Experiments with Potassium Chloride, etc.

On adding potassium chloride to a hot aqueous solution of manganous chloride, sufficiently concentrated to deposit crystals on cooling, a considerable amount of the alkali chloride is dissolved. When the solution cools crystals of a double chloride are deposited, which are pale pink in color, and usually form radiating groups. The individual crystals are elongated and very thin as produced in this way; but by spontaneous evaporation of the solution they can be obtained in much larger form. They are very soluble in water, but cannot be recrystallised in the ordinary sense of the term, for their solution gives a deposit of potassium chloride only, until the manganous chloride is present in large excess. This decomposition of the salt occurs in the same way in the presence of hydrochloric acid, and seems to depend merely on the different solubilities of the two constituents.

The salt is deliquescent in moist air, and was therefore dried in a desiccator over calcium chloride before analysing. It seems to retain its water of crystallisation under these conditions, though a slow loss in weight continues, probably due to the giving up of two molecules of water of crystallisation by the manganous chloride mechanically mixed with the salt. The presence of this manganous chloride accounts for the lack of agreement between the percentage composition found and that calculated. As manganous chloride retains one molecule of water at 110°, the analysis of the salt could not be expected to give figures adding up quite to 100 per cent.

The method used for the determination of the potassium and manganese was as follows: The manganese was precipitated as carbonate by means of ammonium carbonate and then burned to mangano-manganic oxide, while the filtrate was evaporated and the potassium weighed as chloride, after subliming off the ammonium chloride. The same method was used in the case of the rubidium and cæsium salts. Here it has the great advantage of giving the alkali metal back again in the desired form. The precipitation of manganese by ammonium carbonate was found to be almost absolutely complete. Where the filtrate containing the alkali chloride was evaporated in glass vessels, a blank experiment, performed under similar conditions, gave the amount of glass dissolved, which was then deducted.

0.4562 gram salt gave 0.1479 gram Mn_3O_4 (23.35 per cent. Mn), and 0.1415 gram KCl (16.27 per cent. K).

0.2969 gram salt gave 0.5388 gram AgCl (44.88 per cent. Cl.)

0.2517 gram salt lost at 105°–110° 0.0381 gram $H_2O = 15.14$ per cent. H_2O.

	Calculated.		Found.
K	39.03	16.55	16.27
3Cl	106.11	44.99	44.88
Mn	54.8	23.23	23.35
$2H_2O$	35.92	15.23	15.14
	235.86	100.00	99.64

The salt has therefore the formula $KMnCl_3.2H_2O$. It has not been previously described. All efforts to obtain a salt containing a larger proportion of potassium chloride failed. No iodide or fluoride of manganese and potassium was obtained, nor was a bromide obtained by itself, though the substance described below may be regarded as containing a simple double bromide.

Efforts were made to produce, if possible, mixed salts (a chlorbromide and a chlor-iodide) of definite composition. These experiments will now be described.

If a hot, saturated solution of manganous chloride be saturated with potassium bromide and then allowed to cool, crystals are deposited exactly similar in appearance to those of the salt $KMnCl_3.2H_2O$, but containing a considerable amount of bromine. On evaporation of the solution further deposits of crystals can be obtained. The percentage of bromine was found to vary in different crystallisations, as shown by the following analyses, the first being of a very early deposit and the second of a much later one:

I. 0.7380 gram of the salt was dissolved in 500 cc. of water and divided into two equal parts. In each portion the chlorine was precipitated as silver chloride, one of the precipitates being collected and weighed in a Gooch crucible, while the other was reduced to metallic silver in a current of hydrogen.

0.3690 gram gave 0.6621 gram $AgCl + AgBr$, and 0.4823 gram Ag. Hence $Br = 0.03836$ gram $= 10.40$ per cent., and $Cl = 0.14144$ gram $= 38.33$ per cent.

II. The amount of silver which a given weight of the salt would precipitate was determined volumetrically (by Mohr's method), and, in a separate portion, the weight of the mixed precipitates formed from a given amount of the salt was determined. This method is more rapid than the one previously mentioned, but the results are probably less accurate.

0.3134 gram salt gave 0.5434 gram $AgCl + AgBr$, and 0.3238 gram precipitated 0.40001 gram Ag. Hence $Br = 0.0521$ gram in 0.3134 gram salt $= 16.62$ per cent., and $Cl = 0.1041$ gram in 0.3134 gram salt $= 33.22$ per cent.

III. A complete analysis was made of a deposit intermediate between the two just given:

0.4719 gram lost at 105°–110° 0.0671 gram $H_2O = 14.22$ per cent. H_2O, and gave 0.1564 gram K_2SO_4 (14.88 per cent. K), and 0.1395 gram Mn_3O_4 (21.29 per cent. Mn).

0.3426 gram gave 0.5966 gram $AgBr + AgCl$, and 0.3133 gram precipitated 0.3916 gram Ag. Hence $Br = 14.53$ per cent., and $Cl = 34.62$ per cent. In this case the potassium was weighed as sulphate, to ensure the absence of bromine.

The above analyses show that the substance obtained is not a definite compound, but, in all probability, an isomorphous mixture of two salts. It was found by calculation that the mixture might consist of 77.2 per cent. $KMnCl_3.2H_2O$ with 22.8 per cent. $KMnBr_3.2H_2O$, or, supposing the mixed salts to exist, of 48.05 per cent. $KMnCl_3.2H_2O$ with 51.95 per cent. $KMnCl_2Br.2H_2O$.

	Calculated for both mixtures.	Found.
Cl	34.73	34.62
Br	14.78	14.53
Mn	21.32	21.29
K	15.19	14.88
H_2O	13.98	14.22
	100.00	99.54

As the substance comes out of a solution containing a large excess of manganous chloride, as well as some manganous bromide, the agreement between the calculated composition and that found can hardly be expected to be very close. The fact that the salt $KMnBr_3.2H_2O$ was not obtained in the experiments with the pure bromides might be considered as an argument in favor of the belief that the constituent containing bromine in this mixture was really some *mixed* salt, such as $KMnCl_2Br.2H_2O$. However, the explanation that the presence of the salt $KMnCl_3.2H_2O$ gives crystallising power to the salt $KMnBr_3.2H_2O$, so that the two can form an isomorphous mixture, involves perhaps less speculation.

When potassium iodide was used instead of the bromide, in attempting to prepare a mixed salt, crystals of the same habit as before were obtained. A complete analysis of these was made, and the salt was found to contain an amount of iodine so small that it must be considered as a non-essential constituent, present merely by the adhering of a certain amount of mother-liquor. The salt is too easily soluble to admit of its being washed to any considerable extent. In no case was so much as 1 per cent. of iodine found. The salt was, in fact, $KMnCl_3.2H_2O$.

These experiments are of interest as showing what large amounts of potassium bromide and iodide are converted into the chloride by being dissolved in a solution of manganous chloride. These crystallisations were all made in neutral solutions so as to avoid the complications, in interpreting the results, which the presence of even a small quantity of acid would have introduced.

On adding excess of potassium chloride to a warm, saturated solution of manganous bromide in water, filtering while hot, and allowing to cool, a deposit of crystals was obtained consisting largely of potassium bromide. The solution was then evaporated and each successive deposit of crystals removed until a point was at length reached where crystals similar to those of $KMnCl_3.2H_2O$ were formed. They contained bromine and manganese, as well as potassium and chlorine. Analysis showed that they did not correspond in composition to any definite simple salt, but were a mixture (probably an isomorphous mixture) of two or more compounds. It is probable that this substance contained the same salts as that produced by adding potassium bromide to a solution of manganous chloride.

A similar experiment using manganous iodide instead of the bromide gave no satisfactory results, manganous iodide being rather too unstable for this work. It was not to be expected, however, that a double salt would be obtained in this experiment, because the composition of the salts already described seems to prove that both manganous chloride and potassium chloride are necessary constituents in every case. The experiments with manganous chloride and potassium iodide showed how readily the chlorine passed over from the manganese to the potassium, so that it does not seem probable that the reverse action would take place to any considerable extent; hence the solution, in the experiment just mentioned, would contain only a very small quantity of manganous chloride, and the formation of a double salt would not be possible.

Crystallography of the salt.—Accurate measurements of the crystals were found very difficult, owing to the softness of the salt and its tendency towards deliquescence. Sufficient information was obtained, however, from the optical properties and measurements of some angles to show that the crystals are triclinic. Individual crystals often show very irregular development. The drawing given (Fig. 3) is merely to show their general shape, as most commonly obtained. As *gliding* is very readily produced in this salt, a sample of it was sent to Prof. Otto Mügge, of the University of Münster, who has been for some time making a special study of that phenomenon. He has kindly undertaken an investigation of the compound.

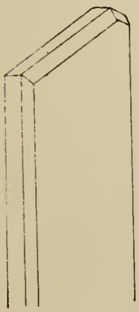
FIG. 3.

Experiments with Ammonium Chloride.

Up to the present time there have been described three compounds of manganous chloride with ammonium chloride:

$NH_4MnCl_3.2H_2O$, described by Hautz;[1]
$(NH_4)_2MnCl_4.H_2O$, described by Rammelsberg[2] and by Pickering;[3]
$(NH_4)_2MnCl_4.2H_2O$, described by v. Hauer.[4]

The directions given by Hautz for the preparation of the salt described by him are simple. A solution of manganous chloride and ammonium chloride, mixed in the proportions required by the formula NH_4MnCl_3, is to be evaporated to crystallisation. These directions being followed, a salt was obtained, which was evidently the same as that described by Hautz. Analysis proved, however, that its formula was not $NH_4MnCl_3.2H_2O$, but $(NH_4)_2MnCl_4.2H_2O$, though the salt as thus produced was not very pure. A pure product was afterwards obtained by mixing the two chlorides in about the proportions mentioned by Hautz, and allowing the aqueous solution to evaporate spontaneously for several months over sulphuric acid. At intervals the deposits of crystals were removed. The fifth sample was found to be pure; the others contained an excess of ammonium chloride.

The analyses of the salt gave the following results:

0.3693 gram gave 0.7870 gram AgCl (52.70 per cent. Cl).

0.3557 gram gave 0.1008 gram Mn_3O_4 (20.41 per cent. Mn).

1.1389 grams lost at 110° 0.1529 gram $H_2O = 13.43$ per cent. H_2O.

0.3015 gram gave 0.04037 gram $NH_4 = 13.39$ per cent. NH_4.

The determination of the water of crystallisation in this salt is of no value. The water is not given off readily, and the anhydrous salt undergoes slow decomposition at 110°. The figures given merely indicate, therefore, the point beyond which the loss of weight was very slow.

	Calculated for $(NH_4)_2MnCl_4.2H_2O$.		Found.
Mn	54.80	20.43	20.41
4Cl	141.48	52.75	52.70
$2NH_4$	36.02	13.43	13.39
$2H_2O$	35.92	13.39	13.43
	268.22	100.00	99.93

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[1] Ann. Chem. (Liebig) **66**, 285.

[2] Pogg. Ann. **94**, 507.

[3] Jour. Chem. Soc., 1879, 654.

[4] J. prakt. Chem. **63**, 436.

The salt usually forms radiating groups of short crystals. It is pale pink in color and of hard texture. It is easily soluble in water, but cannot be obtained very pure by recrystallisation, as it requires the presence of an excess of manganous chloride before it crystallises in quite pure condition. It is not deliquescent in the air, and does not give up its water of crystallisation in a desiccator.

Crystallography of the salt.—Well-developed, individual crystals are not often obtained, and when found, the faces are not, as a rule, bright enough for a satisfactory measurement of the angles with a goniometer. The salt (Fig. 4) is monoclinic in crystallisation, but possesses certain peculiarities due to the fact that two of its axes are almost (if not exactly) equal in length. While the values obtained for these axes are not identical, the difference is quite within the possible error caused by the imperfections of the crystal faces. Owing to the habit of the crystals and the similarity in length of two of the axes, there is some resemblance between crystals of this salt and a rhombic dodecahedron. The cleavage is imperfect. The optical properties show that the crystals are monoclinic. The position of the *b* axis (the axis of symmetry) was determined by the extinction phenomena of the substance.

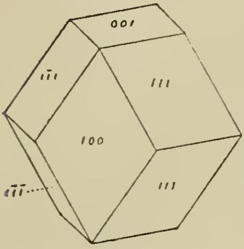

FIG. 4.

The forms observed were 0P, ∞ P $\bar{\infty}$, + P and — P.

Measurements obtained.	Angles calculated.
111 : $\bar{1}11$ = 121° 36½′	121° 37′
111 : $\bar{1}\bar{1}1$ = 90° 16½′	90° 17′
$11\bar{1}$: $\bar{1}11$ = 95° 42′	95° 42′
111 : 100 = 121° 30′	121° 29½′
111 : $11\bar{1}$ = 121° 36½′	121° 48′
$11\bar{1}$: 100 = 117° 43′	116° 53½′
001 : 100 = 95° 25′	95° 25′
111 : 001	121° 26½′
$\bar{1}11$: 001	116° 47½′

These measurements were all made (except the last) from one crystal of the pure salt as used for analysis. The first four measurements were believed to be the best, and were therefore used in calculating the lengths of the axes, and the angle β. They are probably correct within 5′ or 6′. Those lower on the list were not believed to be as good. The constants found were:

$$\grave{a} = 1.4913 \qquad \dot{b} = 1$$
$$\acute{c} = 1.4956 \qquad \angle\beta = 84^\circ\ 35'$$

Hautz describes the salt obtained by him as crystallising in the monoclinic system. The symbols he gives for the forms observed appear to mean that the crystals consisted of a prism, ortho and clino domes, with perhaps one of the pinacoids poorly developed. The symbol of the latter is enclosed in a parenthesis, and it is not clear to which pinacoid it refers. Now, by placing the crystals obtained in this investigation in an incorrect position the forms would become the same as those given by Hautz, except that no plane corresponding to his undetermined pinacoid was observed. The evidence is therefore pretty clear that the two salts are identical. The analyses of Hautz show that the substance as obtained by him was very impure, whatever its formula may have been. He describes the salt as losing 1½ molecules of water at 100°, and the remainder at 135°. It has already been pointed out that determinations of the water in this salt are quite unreliable on account of the tendency to decomposition and the difficulty with which the water is driven off at about 110°. The figures given by Hautz are as follows:

	For salt undried.		For salt dried at 100°.	
	Calculated.	Found.	Calculated.	Found.
NH_4	8.32	8.2	9.84	...
Mn	25.90	...	29.54	28.69
Cl	49.12	...	55.76	55.52
H_2O	16.66	17.4	4.86	4.09
	100.00		100.00	

These figures would be somewhat different if calculated on the basis of the atomic weights now in use; but even then the lack of agreement between the numbers calculated and those found by analysis would be too great, in some cases, to be attributed to errors of experiment. From these partial analyses Hautz derives the formula (using our present atomic weights) $NH_4MnCl_3.2H_2O$ for the undried salt, and $NH_4MnCl_3.\frac{1}{2}H_2O$ for the salt dried at 100°.

It was not found possible to prepare this substance. Even when a large excess of manganous chloride was present in the salt,

$(NH_4)_2MnCl_4.2H_2O$ was invariably obtained. From a consideration of all the evidence, the conclusion is drawn that the salt obtained by Hautz was really $(NH_4)_2MnCl_4.2H_2O$ in an impure condition, and that no salt exists having the formula $NH_4MnCl_3.2H_2O$. This conclusion was quite unexpected, as it was naturally supposed that there would be an ammonium salt corresponding to the potassium salt obtained. The relations between all the members of this series of salts will be referred to farther on.

The salt $(NH_4)_2MnCl_4.2H_2O$, as obtained and analysed by v. Hauer, seems to have been quite impure. He describes it as crystallising in cubes of a yellow or pale red color, which became almost white after recrystallisation. This description is entirely erroneous, except in regard to the pale redness of the salt.

The belief in the existence of the salt $(NH_4)_2MnCl_4.H_2O$ rests on the authority of Rammelsberg and of Pickering. The former states that it crystallises in the regular system, and publishes a partial analysis in proof of the formula given by him. His figures are as follows:

	Calculated.	Found.
Mn	21.97	21.03
4Cl	56.52	...
$2NH_4$	14.34	14.08
H_2O	7.17	...
	100.00	

While the figures obtained in the case of ammonium are fairly close to those calculated, it should be observed that in the case of manganese the figures found are about $\frac{3}{10}$ of a unit nearer to the formula with *two* molecules of water of crystallisation, than to that given by Rammelsberg. Pickering obtained a salt crystallising in hard brown cubes, which after recrystallisation from water gave figures, on analysis, which "corresponded perfectly to the formula" $(NH_4)_2MnCl_4.H_2O$. Unfortunately these figures were not published.

In regard to this salt a series of experiments was carried out, the results of which are here given. The samples analysed were obtained under widely differing conditions.

I. Obtained by rapid cooling of a solution containing manganous chloride and ammonium chloride in proper proportions for the formula $(NH_4)_2MnCl_4$.

0.6610 gram gave 0.0985 gram Mn_3O_4 (10.73 per cent. Mn).
0.2733 gram gave 0.6521 gram AgCl (59.00 per cent. Cl).

II. Obtained by spontaneous evaporation of a solution of the mixed chlorides.

0.3703 gram gave 0.0771 gram Mn_3O_4 (15.00 per cent. Mn).
0.3401 gram gave 0.7668 gram AgCl (55.75 per cent. Cl).

III. A solution was evaporated by heat, and crystallisation allowed to take place by slow cooling.

0.5497 gram gave 0.1161 gram Mn_3O_4 (15.21 per cent. Mn).
0.2974 gram gave 0.6666 gram AgCl (55.43 per cent. Cl).

IV. Prepared by the same method.

0.3355 gram gave 0.0892 gram Mn_3O_4 (19.15 per cent. Mn).
0.2298 gram gave 0.4964 gram AgCl (53.42 per cent. Cl).

V. Obtained by the spontaneous evaporation of a solution containing a large excess of manganous chloride.

0 3557 gram gave 0.1008 gram Mn_3O_4 (20.41 per cent. Mn).
0.3693 gram gave 0.7870 gram AgCl (52.70 per cent. Cl).

VI and VII. These are analyses of the precipitate first mentioned by Godeffroy,[1] which is produced when a saturated solution of manganous chloride in concentrated hydrochloric acid is added to a similar solution of ammonium chloride. As this precipitate had not been previously analysed, it was hoped that it might prove to be a definite compound. It is, however, a mixture of varying composition. Of the two samples obtained, the color of the second was much more decidedly pink than that of the first. They were both dried on a porous plate, and then to constant weight over caustic potash.

VI. Precipitated by mixing solutions at ordinary temperatures.

0.3432 gram gave 0.1056 gram Mn_3O_4 (22.19 per cent. Mn).
0.3112 gram gave 0.6572 gram AgCl (52.22 per cent. Cl).

VII. Precipitated by mixing solutions previously cooled to about 0°.

0.3667 gram gave 0.1202 gram Mn_3O_4 (23.61 per cent. Mn).
0.3592 gram gave 0.7367 gram AgCl (50.72 per cent. Cl).

These results form a series in which the percentage of manganese increases and that of chlorine decreases, as here arranged:

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[1] Ber. d. chem. Ges. **8**, 9.

	Mn.	Cl.
I.	10.73	59.00
II.	15.00	55.75
III.	15.21	55.43
IV.	19.15	53.42
V.	20.41	52.70
VI.	22.19	52.22
VII.	23 61	50.72

The calculated percentages for the formula $(NH_4)_2MnCl_4.H_2O$, using accurate atomic weights, are Mn 21.90 and Cl 56.53. It is evident that no such salt was obtained. Only one substance in the above list was a definite compound, namely the fifth, already described as the salt $(NH_4)_2MnCl_4.2H_2O$. Its crystalline form was definite. I, II and III formed indefinite masses of ill-defined crystals. VI and VII were amorphous precipitates. IV crystallised, at least in part, in perfectly definite octahedrons. As the analysis showed it to be a mixture, it appears highly probable that the octahedrons consisted of impure ammonium chloride, while the remainder of the deposit contained a large amount of the double salt with *two* molecules of water. This might account for the fact that both Rammelsberg and Pickering state that the salt obtained by them is regular in crystallisation. Pickering obtained cubes. It seems probable that in some of the other specimens recorded in the above list manganous chloride was present as a mechanical admixture. As no definite directions are given for the preparation of the salt described by Rammelsberg and by Pickering, absolute proof of its non-existence can hardly be expected. The investigation above related seems, however, to give sufficient proof. It is to be remembered that the only published analytical evidence which is really in favor of the existence of the salt consists of one determination of the ammonium.

From the results obtained in this work with ammonium chloride, the conclusion is drawn that only one compound of that substance with manganous chloride has ever been found, namely the salt $(NH_4)_2MnCl_4.2H_2O$.

Experiments with Rubidium Chloride.

According to R. Godeffroy,[1] rubidium chloride forms with manganous chloride two compounds, differing, however, only in the amount of water of crystallisation contained in them. One is described as a pale rose-red, crystalline powder, having the composition represented by the formula Rb_2MnCl_4. By recrystallising this precipitate, crystals of the formula $Rb_2MnCl_4.3H_2O$ are said to be obtained. The precipitate was here investigated first. It is obtained by bringing together concentrated solutions of manganous chloride and of rubidium chloride, concentrated hydrochloric acid having been used as the solvent in both cases. The precipitate was prepared several times under slightly different conditions of temperature. In every case it was dried according to the method already described under the experiments with ammonium chloride. On subsequent heating to about 105° in an air-bath, every specimen was found to give up water of crystallisation. Partial analyses of three of the samples are here recorded:

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[1] Archiv der Pharmacie [3] **12**, 47; Zeitschr. des allg. österreichischen Apotheker-Vereins, 1875, 21.

I. 2.6691 grams lost at 105°–110° 0.2395 gram $H_2O = 8.97$ per cent. H_2O.

II. 0.5120 gram lost at 105°–110° 0.0537 gram $H_2O = 10.49$ per cent. H_2O.

III. 1.3399 grams lost at 105°–110° 0.1705 gram $H_2O = 12.72$ per cent. H_2O.

The precipitates thus dried were found to contain varying amounts of chlorine.

I. 0.3464 gram gave 0.5408 gram AgCl (38.61 per cent. Cl).
II. 0.3124 gram gave 0.5066 gram AgCl (40.10 per cent. Cl).
III. 0.3216 gram gave 0.5591 gram AgCl (42.99 per cent. Cl).

If these percentages of chlorine be calculated back so as to represent percentages in the salt *before* the combined water was driven off, they become—

I. 35.15 per cent. Cl.
II. 35.89 per cent. Cl.
III. 37.52 per cent. Cl.

All the precipitates were very pale pink in color, the tint being, however, noticeably darker in the case of the third than in the others.

The figures obtained by Godeffroy are as follows:

	Calculated for Rb_2MnCl_4.	Found.
4Cl	38.71	38.48
Mn	14.95	14.00
2Rb	46 34	45.97
	100.00	98.45

From a consideration of all the above facts the conclusion is drawn that the precipitate produced by mixing concentrated solutions of manganous chloride and rubidium chloride in concentrated hydrochloric acid is not anhydrous and is not a single, definite chemical compound, but a mechanical mixture of variable composition. These conclusions harmonise with those arrived at in studying the similar precipitate produced in the case of ammonium chloride.

When the precipitate is dissolved in water and the solution evaporated, extremely pale, pink crystals are obtained, usually forming radiating groups. This substance Godeffroy found to have the composition represented by the formula $Rb_2MnCl_4.3H_2O$, the salt losing two molecules of water at 100° and the remainder at 150°. After working on this salt for some time it was found that it encloses a considerable amount of water mechanically, which is only given off with extreme slowness in a desiccator, unless the salt has been previously thoroughly powdered. Godeffroy does not mention having taken this precaution, and it therefore seems probable that it was partly owing to the error introduced at this point that his analysis led to the formula with three molecules of water instead of the correct one with only two. At 150° the manganous chloride would become partly oxidised, and thus an additional loss in weight—and an additional error—would be obtained. Godeffroy's figures are here given:

	Calculated for $Rb_2MnCl_4.3H_2O$.	Found.
2Rb	40.53	...
Mn	13.03	13.17
4Cl	33.65	33.83
$2H_2O$	8.76	8.54
H_2O	4.03	3.54
	100.00	

In the present investigation the following figures were obtained, the salt having been dried to constant weight, in powdered condition, over calcium chloride:

0.3589 gram gave 0.5099 gram AgCl (35.13 per cent. Cl), and 0.0677 gram Mn_3O_4 (13.59 per cent. Mn).

0.2856 gram lost at 105°–110° 0.0259 gram $H_2O = 9.07$ per cent. H_2O, and gave 0.1707 gram RbCl (42.24 per cent. Rb).

	Calculated for $Rb_2MnCl_4.2H_2O$.		Found.
2Rb	170.4	42.33	42.24
Mn	54.8	13.61	13.59
4Cl	141.48	35.14	35.13
$2H_2O$	35.92	8.92	9.07
	402.60	100.00	100.03

The composition of the salt, therefore, corresponds to that required by the formula $Rb_2MnCl_4.2H_2O$. It is easily soluble in water and can be recrystallised. It readily loses all its water of crystallisation at 110°. It does not deliquesce in the air, and does not lose its water of crystallisation when placed over calcium chloride. This latter point needs, perhaps, further discussion in consideration of the method used for drying the salt for analysis. In the first place it is to be noted that the salt can be dried in ordinary dry air, provided it is in a finely powdered condition, though the process is more rapid over calcium chloride. That the water given off in this drying is not water of crystallisation is clear from three considerations: 1st. it varies in amount; 2d. on examining a crystal of the salt under a microscope, inclusions of water can be seen; 3d. a crystal does not lose its form or transparency when dried over calcium chloride.

Efforts to obtain a salt corresponding to $KMnCl_3.2H_2O$ were made, but no such rubidium salt was found even when a considerable excess of manganous chloride was present. This investigation shows that, in all probability, the only definite compound of manganous chloride with rubidium chloride which is capable of isolation is the salt $Rb_2MnCl_4.2H_2O$.

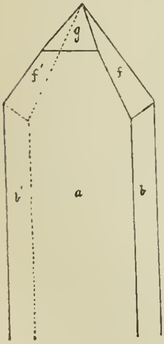

FIG. 5.

Crystallography of the salt.—It is obtained best by spontaneous evaporation of the aqueous solution. The crystals frequently form radiating groups. When well developed they form elongated tabular crystals. In habit they are not always the same, though a common type is that represented in Fig. 5. This consists of two individuals twinned and united along a plane running parallel to the long axis of the crystal. The crystallisation is triclinic, as shown by the optical properties and measurements of the angles. There is no reëntrant angle formed where the two parts of the twin unite, hence the composition face is not a crystallographic plane. The substance shows gliding phenomena. Its crystallography was not worked out in full. The measurements made are, however, pretty accurate, and it is believed that they, together with the rough drawing, will be sufficient for the satisfactory identification of the salt at any time. The cleavage is well marked parallel to the plane *b*.

The following values were obtained by measurement:

$a : b = 84° 57'$.

$a : b' = 95° 5'$.

$a : f = 104° 41'$.

$a : f' = 75° 16'$.

$f : f_1$ (over summit) $= 70° 36\frac{1}{2}'$.

$a : g = 169° 27'$.

$b : f = b' : f' = 138° 40\frac{1}{2}'$ or $141° 42'$. The presence of vicinal planes made the true value of this angle uncertain. The plane *g* does not occur on the other side of the crystal at the same end. Good doubly-terminated crystals were not obtained.

Experiments with Cæsium Chloride.

In the papers already referred to, Godeffroy claims to have found three distinct compounds of manganous chloride with cæsium chloride, namely, a precipitate Cs_2MnCl_4 and two crystalline salts $Cs_2MnCl_4.3H_2O$ and $2(Cs_2MnCl_4).5H_2O$. The precipitate is obtained under the same conditions as were mentioned in the case of ammonium chloride. The substance was prepared three times in slightly different ways, and a partial analysis was made in each case. On drying the precipitate, as in the previous experiments, over caustic potash, a constant weight was not obtained even after a period of two weeks. It is evident that this loss was due to the slow abstraction of water of crystallisation. The determinations of the combined water are necessarily approximate only. The salt was dried first on a porous plate, and then for a few hours over caustic potash before the determination was made

I. Solutions slightly warmed at the time of precipitation:

0.6935 gram lost at 105°–110° 0.0804 gram $H_2O = 11.59$ per cent. H_2O.

After thus drying, 0.3116 gram gave 0.0805 gram Mn_3O_4 (18.61 per cent. Mn), and 0.3001 gram gave 0.4375 gram AgCl (36.05 per cent. Cl).

II. Solutions cooled to about 0° at the time of precipitation:

0.8523 gram lost at 105°–110° 0.0922 gram $H_2O = 10.82$ per cent. H_2O.

After thus drying, 0.3242 gram gave 0.0843 gram Mn_3O_4 (18.73 per cent. Mn), and 0.03416 gram gave 0.4991 gram AgCl (36.13 per cent. Cl).

III. The solution of manganous chloride was quite dilute, the acid in which it was dissolved being, as before, concentrated.

1.1491 grams lost at 105°–110° 0.1189 gram $H_2O = 10.35$ per cent. H_2O.

After thus drying, 0.3589 gram gave 0.0925 gram Mn_3O_4 (18.56 per cent. Mn), and 0.3032 gram gave 0.4432 gram AgCl (36.15 per cent. Cl).

	Calculated for $CsMnCl_3.2H_2O$.	Found.		Calculated for $CsMnCl_3$.	Found.
$2H_2O$	10 90	11.59	Mn	18.66	18.61
		10.82			18.73
		10.35			18.56
			3Cl	36.14	36.05
					36.13
					36.15

The precipitate consists therefore of the salt $CsMnCl_3.2H_2O$ in almost pure condition. After drying in an air-bath at 105° its composition corresponds to the formula $CsMnCl_3$. No compound of cæsium chloride with manganous chloride in these proportions has hitherto been described. The results which Godeffroy obtained by analysis of the precipitate, prepared in the same way as the above, are:

	Calculated for Cs_2MnCl_4.	Found.
2Cs	57·47	57·76
Mn	11.87	11.11
4Cl	30.66	31.04
	100.00	99·91

He seems to have analysed the salt only once. He does not state the manner in which the precipitate was dried. No explanation is here offered to account for the disagreement between these results and those obtained in the present investigation, but the author feels compelled to conclude that there was some serious error in the work of Godeffroy.

The pale pink precipitate just described is easily soluble in water. When the solution is evaporated, crystals are obtained belonging to the orthorhombic system. These can be recrystallised and are then found to be in pure condition. The salt is pale pink in color. It is not deliquescent in the air under ordinary conditions; but, when powdered, it loses its water of crystallisation in a good desiccator over calcium chloride. This loss, which is very slow, has already been referred to in the case of the impure, precipitated salt. It gives up its water of crystallisation very readily at 105°. For analysis the salt was dried by pressure between layers of filtering paper.

0.5028 gram lost at 105° 0.0548 gram $H_2O = 10.90$ per cent. H_2O.

The dried salt was then analysed.

0.4212 gram gave 0.1092 gram Mn_3O_4 (18.67 per cent. Mn), and 0.2416 gram CsCl (45.29 per cent. Cs).

0.4480 gram gave 0.6547 gram AgCl (36.14 per cent. Cl).

	Calculated for $CsMnCl_3.2H_2O$.	Found.
$2H_2O$	10.90	10.90

	Calculated for $CsMnCl_3$.		Found.
Cs	132.7	45.20	45.29
Mn	54.8	18.66	18.67
3Cl	106.11	36.14	36.14
	293.61	100.00	100.10

The crystallised salt has therefore the formula $CsMnCl_3.2H_2O$, and loses all of its water at 105°.

Crystallography of the salt.—The substance forms tabular crystals, which are shown by their optical properties and angular measurements to be orthorhombic (Fig. 6). The forms observed were, $0P$, $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, ∞P and $P\breve{2}$. The reflections obtained in the goniometer were not, as a rule, very good, and the exact values of the angles are rendered additionally doubtful in some cases, owing to the presence of vicinal planes.

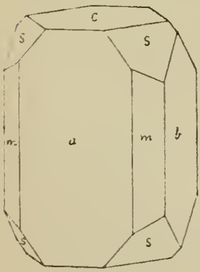

FIG. 6.

$c = 0P$, [001].
$a = \infty P\bar{\infty}$, [100].
$b = \infty P\breve{\infty}$, [010].
$m = \infty P$, [110].
$s = P\breve{2}$, [122].

By comparing together many measurements the following values were obtained, which appeared sufficiently trustworthy for the determination of the axial ratios :

$s:a=116^\circ\ 14'$.
$s:c=124^\circ\ 7'$.
$s:s=127^\circ\ 32'$.
$m:b=128^\circ\ 6'$.
$m:a=141^\circ\ 54'$.

The axial ratios deduced are $\breve{a}=.7919$, $\bar{b}=1$, $\acute{c}=1.2482$.

When the angles given above are calculated from these axial ratios they become :

$s:a=116^\circ\ 14'$.
$s:c=124^\circ\ 7'$.
$s:s=127^\circ\ 32'$.
$m:b=128^\circ\ 22\frac{1}{2}'$.
$m:a=141^\circ\ 37\frac{1}{2}'$.

The cleavage is parallel to *a*.

If cæsium chloride be added to a solution of the salt $CsMnCl_3.2H_2O$, crystals are deposited, on evaporation, which are quite different in habit from those previously obtained, and are much paler in color. These proved to be the salt corresponding to that obtained when working with rubidium chloride, having the formula $Cs_2MnCl_4.2H_2O$. This is probably the compound obtained by Godeffroy and regarded by him as two different salts, namely $Cs_2MnCl_4.3H_2O$ when crystallised out of an aqueous solution, and $2(Cs_2MnCl_4).5H_2O$ when crystallised out of a solution in concentrated hydrochloric acid. The salt is not deliquescent in ordinary air, and retains its water of crystallisation when dried in an ordinary desiccator. For analysis it was dried, in the form of a fine powder, over calcium chloride. Its water of crystallisation is readily driven off at 105°.

0.4311 gram gave 0.0663 gram Mn_3O_4 (11.08 per cent Mn), and 0.2923 gram CsCl (53.53 per cent. Cs).

0.2204 gram lost at 105° 0.0162 gram $H_2O=7.35$ per cent. H_2O, and gave 0.2532 gram AgCl (28.41 per cent. Cl).

	Calculated for $Cs_2MnCl_4.2H_2O$.		Found.
2Cs	265.4	53.34	53.53
Mn	54.8	11.01	11.08
4Cl	141.48	28.43	28.41
$2H_2O$	35.92	7.22	7.35
	497.60	100.00	100.37

The salt corresponds in composition to the formula $Cs_2MnCl_4.2H_2O$. Godeffroy's analyses of this salt, which seemed to indicate the presence of three molecules of water, were no doubt vitiated by the incomplete drying of the salt before analysis, as was pointed out in the case of the corresponding rubidium compound. His figures are:

	Calculated for $Cs_2MnCl_4.3H_2O$.	Found.
2Cs	51.39	...
Mn	10.65	10.07
4Cl	27.50	27.24
$3H_2O$	10.46	10.96 and 10.23
	100.00	

No evidence was found in favor of the existence of a salt of this composition.

Crystallography of the salt $Cs_2MnCl_4.2H_2O$.—This was not worked out in full, but the following details are given to serve for the identification of the substance. It is triclinic in crystallisation, resembling, in general appearance, the corresponding rubidium salt. The cleavage is, however, parallel to the best developed face, *a*, which is not true of the rubidium compound. Another difference between the two salts is observed in regard to the method of twinning. The cæsium salt shows a reëntrant angle of about 169° where the two individuals are joined, while the rubidium salt does not. Other differences are evident from the measurements. Fig. 7 gives a rough drawing of a crystal of this salt, not twinned. Most of the measurements here given are the mean of two, made on different crystals. They generally agreed within a few minutes. The last two are only approximate. The plane *g* occurs only on one side of the crystal at each end.

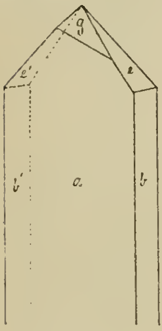

FIG. 7.

The following measurements were obtained:

$a : b = 95° 27'$ (hence $a : b' = 84° 33'$).
$a : g = 139° 24'$.
$b : e = 151° 6'$.
$b' : e' = 154° 1\frac{1}{2}'$.
$e : e'$ (over summit) $= 54° 53\frac{1}{2}'$.
$a : e = 85\frac{3}{4}°$.
$a : e' = 97\frac{1}{4}°$.

A careful attempt was made to prepare the salt $2(Cs_2MnCl_4).5H_2O$ by following the directions of Godeffroy as closely as possible. The solution in concentrated hydrochloric acid, which remained over the precipitate of slightly impure $CsMnCl_3.2H_2O$, was evaporated without the aid of heat, by drawing a stream of dry air over it for several months. A few small crystals were at length obtained. These were very pale pink in color and seemed to be the salt $Cs_2MnCl_4.2H_2O$. On attempting to isolate the compound, after further evaporation of the solution, it was found that some other substance, probably manganous chloride, had crystallised out as well. As it was evidently impossible to obtain a pure product without recrystallisation, which would have been to depart from the conditions mentioned by Godeffroy, the subject was not followed up. In view of the existence of the salt $Cs_2MnCl_4.2H_2O$, and of the non-existence of the salt $Cs_2MnCl_4.3H_2O$ described by Godeffroy, and in view of the weak evidence brought forward to prove the existence of the salt $2(Cs_2MnCl_4).5H_2O$, the matter did not seem worthy of further investigation. The existence of the salt under consideration seems in the highest degree improbable.

Experiments with Magnesium Chloride and with Magnesium Bromide.

In this part of the work it was found more satisfactory to use alcohol and water, instead of water alone, as a solvent. Seventy per cent. of alcohol is probably about the best strength. The solutions were always kept acidified to prevent the decomposition of the magnesium salt. When a solution of manganous chloride and magnesium chloride is evaporated the two chlorides unite, forming one or, perhaps, more compounds, the appearance of which varies greatly according to the exact conditions of formation. Many experiments were performed. In general a compound was obtained crystallising in flattened, sometimes feather-like crystals, which were never found to be pure. On one occasion these plates were left standing for several weeks in contact with the mother-liquor, and were found to be entirely transformed into crystals almost round in shape, usually about ½ cm. in diameter. They could not be investigated crystallographically, owing to their rapid deliquescence. Though not obtained in pure condition, analysis shows that this salt corresponds in composition to the bromide, described below, which is much more easily worked with. The flattened crystals of the chloride seem to have the same composition as the rounded ones, though they were never obtained in a condition approaching purity. As this double chloride, in whatever form it is obtained, is deliquescent in the air and loses some of its water of crystallisation over calcium chloride, a satisfactory analysis of it could not be made. It was dried for a few hours in a desiccator, but was found when analysed to contain, still, a considerable amount of hygroscopic water. For the method of analysis see below.

0.7608 gram gave 0.1981 gram Mn_3O_4 (18.76 per cent. Mn), and 0.1569 gram $Mg_2P_2O_7$ (4.50 per cent. Mg).

0.9970 gram gave 1.4961 grams AgCl (37.11 per cent. Cl).

The water of crystallisation is not all given off without decomposition of the salt.

	Calculated for $Mn_2MgCl_6.12H_2O$.		Found.
2Mn	109.6	19.52	18.76
Mg	24.21	4.31	4.50
6Cl	212.22	37.79	37.11
$12H_2O$	215.52	38.38	...
	561.55	100.00	

If we allow for the hygroscopic water, which seems to be present, 1¼ per cent., we obtain Mn 19.15, Mg 4.59 and Cl 37.88 per cent. The salt, though somewhat impure, evidently corresponds in composition to the bromide mentioned below, and has the formula $Mn_2MgCl_6.12H_2O$.

As noticed near the commencement of this paper, when a large excess of manganous chloride is present the salt $Mn_2Cl.2H_2O$ is produced. No evidence was found of the existence of a salt containing manganous chloride and magnesium chloride in the proportions of one molecule to one.

When manganous bromide and magnesium bromide are present in a solution in the proportion of two molecules of the former to one of the latter, and the solution is evaporated, a double salt crystallises out on cooling. The substance usually forms a compact mass of red crystals at the bottom of the beaker. It can be recrystallised, but well-formed, individual crystals are seldom obtained. It is deliquescent in the air. No loss of water of crystallisation was observed when it was dried over calcium chloride. The most convenient method found for the separation of the metals, in analysis, was as follows: Decompose the salt with a small amount of sulphuric acid, and heat till all the hydrochloric (or hydrobromic) acid is driven off; then add a solution of ammonium chloride, and heat nearly to boiling. Add gradually ammonium sulphide free from carbonate. Keep hot for about an hour, and then filter and wash. The manganous sulphide is then dissolved in dilute hydrochloric acid, filtered free from sulphur, and precipitated as carbonate after driving off the hydrogen sulphide. The solution containing the magnesium is evaporated, acidified, filtered from sulphur, and the magnesium then precipitated in the usual way.

The water of crystallisation present in this salt cannot be determined directly on account of the decomposition of the substance. That decomposition actually takes place before all the water is given off is evident from the darkening in color, and the fact that part of the salt is rendered insoluble in water. The substance was obtained in almost pure condition without recrystallisation, as shown by the following figures obtained:

0.6679 gram gave 0.1235 gram Mn_3O_4 (13.32 per cent. Mn), and 0.0915 gram $Mg_2P_2O_7$ (2.99 per cent. Mg).

0.6654 gram gave 0.8998 gram AgBr (57.55 per cent. Br).

After heating the salt for several hours not far above 100°, and then for seven hours at about 150°, the loss in weight represented 16.27 per cent. of water. Considerable decomposition had taken place.

	Calculated for $Mn_2MgBr_6.12H_2O$.		Found.
2Mn	109.6	13.24	13.32
Mg	24.21	2.93	2.99
6Br	478.56	57.80	57.55
$12H_2O$	215.52	26.03	...
	827.89	100.00	

The formula of the salt is therefore $Mn_2MgBr_6.12H_2O$, corresponding to that of the impure chloride obtained.

Negative Results.

No compound of lithium chloride with manganous chloride was found, but it is worthy of note that the aqueous solution of the mixed chlorides has, when concentrated, a *green* color, which becomes quite brilliant when the solution is heated. When potassium chloride is present instead of lithium chloride, the hot solution appears greenish-brown.

Some evidence of the formation of a compound of sodium chloride with manganous chloride was obtained, but it was not found possible to isolate the product in sufficiently pure condition for analysis, owing to the very great excess of manganous chloride present.

Unsuccessful attempts were made to obtain compounds of manganous chloride with the chlorides of copper (cuprous and cupric), calcium, strontium and barium. A concentrated solution of the mixed chlorides of calcium and manganese possesses a green color, somewhat like that observed in the case of lithium chloride. An almost amorphous mass was obtained, containing manganous chloride and calcium chloride, which may have been an impure double salt, but it was not in a fit condition for analysis.

Conclusion.

The work was not continued beyond magnesium. Compounds have, however, been described of manganous chloride with cadmium chloride[1] and with mercuric chloride.[2] We find, then, that manganous chloride combines with the chlorides of potassium, rubidium and cæsium; but that, following the families according to the periodic system, there is, after cæsium, a gap of considerable length, including chiefly the chlorides of calcium, strontium and barium. Manganous chloride appears incapable of combining with any of the chlorides between cæsium and magnesium. The latter, however, marks the commencement of a new series, with every member of which manganous chloride can probably combine. The explanation of these facts is simple if we assume that the acidic and basic powers of manganous chloride are about equal to those of strontium chloride, and that in its compounds with the chlorides of potassium, rubidium and cæsium, manganous chloride acts in its acidic capacity, while in its compounds with the chlorides of magnesium (zinc?), cadmium, etc., it acts in its basic capacity. Taking this view we should expect a break to occur between these two series.

The compounds hitherto described are given in tabular form at the commencement of the paper. A comparison between that list and the one given below, of the compounds actually found to exist, will show that the regularity in the series is much greater than was to be supposed.

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[1] v. Hauer, J. prakt. Chem. **68**, 393.

[2] v. Bonsdorff, Pogg. Ann. **17**, 247.

$KMnCl_3.2H_2O$ (tricl.)	———
———	$(NH_4)_2MnCl_4.2H_2O$ (monocl.)
———	$Rb_2MnCl_4.2H_2O$ (tricl.)
$CsMnCl_3.2H_2O$ (orthorh.)	$Cs_2MnCl_4.2H_2O$ (tricl.)

$Mn_2MgCl_6.12H_2O.$

$Mn_2MgBr_6.12H_2O.$

It will be noticed that these salts are very irregular from a crystallographic point of view. It is strange that two gaps should occur in the left-hand series. Special efforts were made to obtain both of the missing compounds, but without success. Perhaps the entire dissimilarity in crystal system and habit between the potassium and the cæsium salt may be taken as evidence that, though chemically analogous, the two compounds are not really very closely related to each other.

IV.—ON SOME DOUBLE HALIDES OF ANTIMONY.[1]

BY CHARLES E. SAUNDERS.

Since two double chlorides containing antimony had been described by Godeffroy as containing six molecules of alkali chloride to one of antimony chloride, and were therefore to be regarded as exceptions to the general rule governing the composition of the double halides, it was thought best to repeat the work of Godeffroy. The exceptional salts referred to are

$$SbCl_3.6CsCl \quad \text{and} \quad SbCl_3.6RbCl.$$

Experiments with Cæsium Chloride.

It is necessary, first of all, to give a brief review of the work of Godeffroy on this subject. In 1874[2] he published the first statements in regard to the precipitate obtained by mixing solutions of antimony chloride and cæsium chloride in concentrated hydrochloric acid. This precipitate was recrystallised several times and analysed. The mean of five analyses gave him the following results:[1] Chlorine, 33.419 per cent.; antimony, 30.531 per cent. From these figures he derives the formula $SbCl_3.CsCl$. The numbers calculated from the formula are: Chlorine, 35.93 per cent.; antimony, 30.37 per cent. Godeffroy regarded the precipitate and the crystalline salt as identical in composition, but gives no definite proof in support of this idea. In the year following[2] he published a complete analysis of the salt, assigning to it an entirely new formula, namely, $SbCl_3.6CsCl$. The results he gives are as follows:

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[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1891.

[2] Zeitschr. des allg. österr. Apotheker-Vereins, 1874, 161.

Calculated for $SbCl_3.6CsCl$.		Found.
9Cl	25.77	25.68
Sb	9.83	9.40
6Cs	64.40	63.98
	100.00	99.06

While the figures found agree fairly well with those calculated, the fact must not be lost sight of that there is a discrepancy between the figures found in 1874 and those found in 1875 of over seven units in the case of chlorine and of over twenty-one units in the case of antimony. As no explanation of this difference is given, it seems necessary to attribute it to experimental errors in analysis. The methods used in the latter investigation are worthy of notice in this connection. The salt was dissolved in water acidified with tartaric acid, and after precipitation of the chlorine as silver chloride, the antimony was precipitated as sulphide. The sulphide was then oxidised with nitric acid, and the sulphuric acid thus obtained was estimated in the usual way. The amount of antimony was then calculated from the amount of barium sulphate obtained.

In the present investigation the precipitate was prepared in the manner described, the conditions of temperature being, however, slightly varied in the different experiments. The antimony chloride used for the first was purified by precipitation as oxychloride, that for the second by distillation. The precipitate of the double salt is very pale yellow in color. This does not appear to be due to impurities. The crystallised salt has the same color. The precipitates were dried for analysis in the manner before described. The methods of analysis will be referred to later on in the paper.

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[1] Ber. d. chem. Ges. 7, 375.

[2] Zeitschr. des allg. österr. Apotheker-Vereins, 1875, 21.

I. 0.6051 gram gave 0.2146 gram Sb_2S_3 (25.32 per cent. Sb), and 0.3162 gram CsCl (41.26 per cent. Cs).

II. 0.7470 gram gave 0.2682 gram Sb_2S_3 (25.63 per cent. Sb), and 0.3880 gram CsCl (41.01 per cent. Cs).

A third preparation of the precipitate, using the same redistilled antimony chloride as was used for the second, gave 25.38 per cent. of antimony. The composition of the precipitate appears therefore to be nearly constant. The figures obtained correspond pretty closely to those required for a salt of the formula $2SbCl_3.3CsCl$.

	Calculated for $Cs_3Sb_2Cl_9$.	Found.	
Sb	25.03	25.32	25.63
Cs	41.66	41.26	41.01

This precipitate is soluble in hot dilute hydrochloric acid, though only slightly soluble in the cold. On evaporation, crystals of various habits are obtained according to the conditions. They generally appear as needles or thin prisms when deposited by the cooling of a hot solution; while by spontaneous evaporation they form thicker prisms or irregular plates, having a rough pseudo-hexagonal appearance produced by twinning. Two or three different samples of the crystallised salt were analysed. The composition of all of them agreed with the formula proposed:

0.3112 gram gave 0.1641 gram CsCl (41.63 per cent. Cs).

0.1940 gram gave 0.0684 gram Sb_2S_3 (25.16 per cent. Sb).

0.2059 gram gave 0 2770 gram AgCl (33.27 per cent. Cl).

0.4237 gram gave 0.1499 gram Sb_2S_3 (25.25 per cent. Sb), and 0.2240 gram CsCl (41.74 per cent. Cs).

0.2203 gram gave 0.2938 gram AgCl (32 97 per cent. Cl).

	Calculated for $Cs_3Sb_2Cl_9$.		Found.	
3Cs	398.1	41.66	41.63	41.74
2Sb	239.2	25.03	25.16	25.25
9Cl	318.33	33.31	33.27	32.97
	955.63	100.00	100.06	99.96

As this salt was obtained with the greatest ease and according to the method described by Godeffroy, the author feels justified in drawing the conclusion that this is the compound for which Godeffroy proposed the formula $SbCl_3.CsCl$ and, later, $SbCl_3.6CsCl$, the correct formula being $Cs_3Sb_2Cl_9$. This salt is therefore no longer to be considered as an exception to the general rule regarding the composition of the double halides. This is the only compound of cæsium chloride and antimony chloride which is easily obtained. It may be that a salt of the formula $CsSbCl_4$ could be produced under suitable conditions, but the salt above described was the only one identified in the present investigation, though efforts were made to obtain others.

The crystallography of this salt was not worked out. A few details were, however, obtained. It usually crystallises in elongated prisms. These belong to the orthorhombic system, but are sometimes twinned, when very short, in such a way as to give a rough pseudo-hexagonal form. Such a twin is represented in Fig. 8. The three individuals combined in the crystal can be distinguished by examination in parallel polarised light.

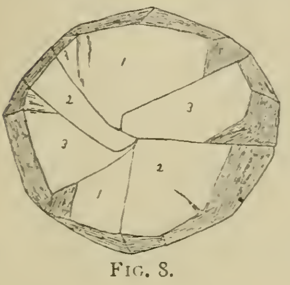

FIG. 8.

Experiments with Rubidium Chloride.

By evaporation of a dilute hydrochloric acid solution containing antimony chloride and rubidium chloride, Godeffroy[1] obtained tabular crystals of a double salt, to which he gave the formula $SbCl_3.6RbCl$. This was analysed by the same method as that described under cæsium chloride. The following are the figures given by Godeffroy:

	Calculated for $SbCl_3.6RbCl$.	Found.
9Cl	33.47	33.45
Sb	12.79	13.10
6Rb	53.74	53.06
	100.00	99.61

A substance corresponding to Godeffroy's description was easily obtained by following his directions, and crystallised out of the solution in dilute hydrochloric acid in beautiful, colorless, six-sided plates, tables, or thicker crystals, according to the conditions. The salt has a very strong crystallising force. It is readily soluble in dilute hydrochloric acid, but less so in the concentrated acid.

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[1] Zeitschr. des allg. österr. Apotheker-Vereins, 1875, 21.

By mixing concentrated solutions of rubidium chloride and of antimony chloride in concentrated hydrochloric acid, the double salt is formed as a distinctly crystalline precipitate. Repeated analyses show that the composition of this salt does not correspond to the formula proposed by Godeffroy. The substance was prepared under varying conditions, being crystallised out either by slow cooling of the solution, or by sudden cooling, or by spontaneous evaporation. In the first experiment the two chlorides were mixed in the proportions required by the formula of Godeffroy. In the other cases no special care was taken in regard to the proportions. The composition of the salt formed did not vary appreciably. All the analyses made, in this part of the investigation, are here given, except one attempt to determine rubidium as nitrate, which was quite untrustworthy. The variations from the normal composition are no doubt due to experimental errors, or to the presence of slight impurities in some specimens of the salt.

I. 0.5720 gram gave 0.1902 gram Sb_2S_3 (23.73 per cent. Sb), and 0.8538 gram AgCl (36.91 per cent. Cl).

II. 0.4174 gram gave 0.1401 gram Sb_2S_3 (23.96 per cent. Sb), and 0.2297 gram RbCl (38.89 per cent. Rb).

0.3190 gram gave 0.4772 gram AgCl (36.99 per cent. Cl).

III. 0.4028 gram gave 0.1348 gram Sb_2S_3 (23.89 per cent. Sb), and 0.6007 gram AgCl (36.88 per cent. Cl).

0.6881 gram gave 0.3769 gram RbCl (38.71 per cent. Rb).

IV. 0.2728 gram gave 0.4071 gram AgCl (36.90 per cent. Cl).

V. 0.3359 gram gave 0.1125 gram Sb_2S_3 (23.90 per cent. Sb), and 0.1850 gram RbCl (38.92 per cent. Rb).

A tabular view of these results will make the matter clearer.

	Calculated[1] for $SbCl_3.6RbCl$.	Found by Godeffroy.	Found by the Author.			
			I.	II.	III.	IV. and V.
Sb	12.60	13.10	23.73	23.96	23.89	23.90
6Rb	53.86	53.06	...	38.89	38.71	38.92
9Cl	33.54	33.45	36.91	36.99	36.88	36.90

These figures show that the salt obtained in the present investigation is a definite chemical compound, which does not correspond in composition to the numbers calculated from Godeffroy's formula. That this salt is really identical with that obtained by

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[1] These figures differ slightly from those calculated by Godeffroy, owing to the use of different atomic weights in the two cases.

Godeffroy, in spite of the great difference between the analytical results in the two cases, is proved by several considerations. This salt is obtained with the greatest ease, much more readily than any other compound of rubidium chloride with antimony chloride. Of the three salts found this one contains the largest percentage of rubidium, and therefore approaches more nearly than either of the others to the composition required by Godeffroy's formula. The directions of Godeffroy were followed closely in preparing the salt, and in one case at least the two chlorides were present in solution in the proportions required by the above formula. The salt was examined crystallographically by Streng.[1] He describes it as forming hexagonal tables by a combination of the basal plane and fundamental pyramid, with a very slight development of the fundamental prism. In the present investigation no distinct development of the prism was observed. The pyramid faces were strongly striated in a horizonal direction, so that accurate measurements were impossible. The mean of three measurements of P : P over a middle edge gave him 129° 30′, from which he calculated the axial ratio $a:c$ as 1 : 1.836. The crystals obtained in the present investigation agree with the description of Streng. The angle measured by him was here found to vary between 127° and 131°, though the striations on the crystals prevented anything but the roughest measurements. Stauroscopic examination shows that the crystals are not really hexagonal in crystallisation; but as Streng does not seem to have examined his crystals optically, this disagreement in regard to the crystal system cannot be considered as evidence in favor of the two salts being different. The substance as prepared in this investigation was, to all outward appearance, hexagonal in crystallisation, and agreed exactly, except in the points mentioned, with the descriptions given by Godeffroy and by Streng. There can therefore be little doubt that the substances as obtained in the two investigations were identical. The conclusion is therefore drawn that no salt exists having the formula $SbCl_5.6RbCl$.

As the five partial analyses already given showed that the formula of the salt was by no means simple, the matter was taken up again, with a view to obtaining a quantity of the salt in as pure a condition as possible, and then making several analyses. Having prepared a considerable amount of the substance, it was recrystallised five times from dilute hydrochloric acid. In the last two crystallisations the solution was cooled rapidly, so that the salt was deposited in very small, six-sided scales, possessing a beautiful, pure white, lustrous appearance. The final drying of the compound was as follows: It was first of all dried by pressure between layers of filtering paper previously washed with hydrochloric acid, and was then finely powdered and placed on a watch-glass in a desiccator over phosphorus pentoxide. It was weighed from day to day until the loss in twenty-four hours was not perceptible, the weighings being made to the tenth of a milligram. In this way over two grams of the salt were obtained. The methods of analysis used are now to be described. In nearly all the analyses of salts containing antimony, the methods used were essentially the same as those here given.

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[1] Archiv der Pharmacie [3] **9**, 343.

The salt was dissolved in dilute hydrochloric acid in an Erlenmeyer flask and the solution heated to incipient boiling. Carefully washed hydrogen sulphide was then passed in until the solution was nearly cold. The flask was then tightly closed and left for at least an hour, when it was heated again to about 60°. The antimony sulphide was collected in a Gooch crucible, the filtration being performed while the liquid was hot. The precipitate was then washed with freshly prepared hydrogen sulphide water and afterward dried for about an hour at 105°. The crucible was then placed in a small air-bath filled with carbon dioxide, into which a current of the washed and dried gas was kept passing. The temperature of this bath was slowly raised to 200° and the flame then extinguished. The sulphide of antimony obtained in this way was black and anhydrous. It was found that all the water can be driven off from the sulphide without converting it into the black form, but the process is very slow. When the black sulphide was heated to 200°–220° for a few hours a slight loss in weight was observed in almost all cases. This may have been due to the decomposition of a minute quantity of oxychloride of antimony present. One precipitation of the sulphide (the fourth) was made after adding a small quantity of tartaric acid to the solution. The precipitate formed in this case also suffered a very slight loss in weight on continued heating. If the presence of oxychloride of antimony be the cause of this reduction in weight it proves that, under the conditions mentioned, excess of hydrogen sulphide does not entirely decompose oxychloride of antimony, even when acting for so long a time as three hours on the precipitate, the solution being kept warm during one hour. The first weighing of the precipitate was the one assumed to be correct in every case. The subsequent loss in weight was so slight (usually about one-tenth of a milligram in half an hour's heating at 210°), that no great error can have been introduced by neglecting it, whatever may have been its actual cause. The use of carbon dioxide to prevent the presence of oxygen in the solution during or after the precipitation of the antimony sulphide, seems to be quite unnecessary if the above directions be followed.

The rubidium was determined as chloride by evaporation of the filtrate, in which it was contained, in a platinum vessel. Before weighing, it was dried at about 230° and finally heated for a few moments to incipient redness. Special experiments showed that about one-tenth of a milligram of rubidium chloride was lost in the final heating. A correction was therefore made for that loss. The amount of solid matter obtained by the action of the hot solution on the glass during the precipitation of the antimony was determined by a blank experiment under the same conditions. A correction for this gain in weight was introduced in each determination of rubidium.

Chlorine was usually determined by precipitation as silver chloride in a solution of the salt in water acidified with tartaric and nitric acids. The silver chloride was afterwards dissolved in ammonia and reprecipitated. Determination of the chlorine after precipitation of the antimony as sulphide was found extremely difficult. The presence of an excess of free hydrochloric acid seems necessary to bring the antimony sulphide into a condition suitable for filtration.

As the determination of the atomic ratio between antimony and rubidium seemed to promise to give results containing the slightest errors, special stress was laid, in the following analyses, on that ratio. The analyses of the salt gave these results:

I. 0.3844 gram gave 0.1288 gram Sb_2S_3 (23.915 per cent. Sb), and 0.2129 gram RbCl (39.137 per cent. Rb).

II. 0.4401 gram gave 0.1476 gram Sb_2S_3 (23.937 per cent. Sb), and 0.2436 gram RbCl (39.113 per cent. Rb).

III. 0.3936 gram gave 0.1316 gram Sb_2S_3 (23.864 per cent. Sb), and 0.2175 gram RbCl (39.049 per cent. Rb).

IV. 0.3867 gram gave 0.1297 gram Sb_2S_3 (23.939 per cent. Sb).

V. 0.4078 gram gave 0.6115 gram AgCl (37.08 per cent. Cl).

The atomic ratios of antimony to rubidium as deduced from the three analyses are:

I. Sb : Rb as 1 : 2.297.
II. Sb : Rb as 1 : 2.294.
III. Sb : Rb as 1 : 2.297.
Mean Sb : Rb as 1 : 2.296.

From this the following ratios are derived. They are the only ones, at all simple, in which the figures are approximately whole numbers:

Sb : Rb as 4 : 9.184
Sb : Rb as 7 : 16.072
Sb : Rb as 10 : 22.960

The simplest of these ratios, 4 to 9, must be rejected, as the experimental errors due to impurities in the salt or to defects in the analytical methods can hardly have been as great as those which would be indicated by the formula $4SbCl_3.9RbCl$. The figures calculated from the ratios 7 to 16 and 10 to 23 are given below, together with the analytical results obtained by taking the mean of the determinations made with this last sample of the salt. That these results are uniformly higher than those found in the former analyses is probably due to imperfect drying of the salt in the earlier samples. The atomic weights used are Sb 119.6, Rb 85.2, Cl 35.37.

	Calculated for $7SbCl_3.16RbCl$.	Calculated for $10SbCl_3.23RbCl$.	Found.
Sb	23.86	23.776	23.91
Rb	38.85	38.957	39.10
Cl	37.29	37.267	37.08
	100.00	100.000	100.09

It will be seen that the agreement between the calculated composition and that found is closer for the larger formula than for the smaller. Assuming the larger formula to be correct, the disagreement between the figures may be due to errors in analysis, impurities present in the salt, and also perhaps to inaccuracy in the atomic weights used. While it is evidently impossible from these figures to establish the formula of this compound on a firm basis, the analyses prove that the salt is unusually complex in composition, and indicate that the most probable formula is $Sb_{10}Rb_{23}Cl_{53}$.

The salt is extremely stable in some respects. Though easily decomposed by water, as would be expected, it can be heated in an air-bath to a very high temperature without undergoing any appreciable change. At 230° (several degrees above the boiling-point of antimony chloride) it was found to suffer slow decomposition, with loss of weight.

Stauroscopic examination of the salt shows that it is only *pseudo*-hexagonal, being in reality optically biaxial and positive. The acute bisectrix is almost (perhaps quite) normal to the basal plane. The optical behavior of the substance seems to indicate that it is usually composed of a series of superposed plates, with the planes of their optic axes not coincident. In some cases the crystals do not become dark in any position when rotated between crossed nicols. Thinner plates sometimes show an interference figure similar to that produced by two superposed plates of muscovite, with the planes of their optic axes at right angles. The thinnest plates show sharp extinction, and give an interference figure which apparently denotes orthorhombic symmetry. Other plates show a sort of extinction wave or brush, which traverses the crystal when it is rotated between crossed nicols in parallel polarised light. Owing to the striations on the crystals (Fig. 9), no conclusions in regard to the system to which they belonged could be drawn from the measurements of the angles. The cleavage of the salt is basal and well marked.

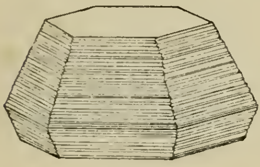

Fig. 9.

Mr. C. P. Brigham, working in this laboratory, has obtained a double salt of bismuth and rubidium chlorides, which, as he has shown, corresponds in formula to the salt above described.[1]

On adding a considerable excess of antimony chloride to a solution of the complex salt discussed above, and evaporating, crystals of an entirely different form are obtained. These were not investigated crystallographically, but may be described as compact crystals, sometimes resembling a rhombohedron in general shape. They are pale yellow in color. This is noteworthy, because the more complex salt (described above) and the simpler one (discussed below) are both colorless. It is to be remembered, however, that the salt $Cs_3Sb_2Cl_9$ is also yellow. As the formula of this rubidium salt is not very simple, and as the substance could not be recrystallised, on account of the strong tendency towards the formation of the very complex salt, the formula suggested below can hardly be considered as definitely established. The analytical results obtained from different samples varied considerably, and it does not appear possible to obtain the salt in pure condition.

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[1] See the following article.

One sample gave the following results:

0.3382 gram gave 0.1348 gram Sb_2S_3 (28.45 per cent. Sb), and 0.1560 gram RbCl (32.60 per cent. Rb).

0.2712 gram gave 0.4217 gram AgCl (38.45 per cent. Cl).

In another sample 0.1530 gram gave 0.2392 gram AgCl (38.66 per cent. Cl).

	Calculated for $3SbCl_3.5RbCl$.		Found.
3Sb	358.8	28.03	28.45
5Rb	426.0	33.28	32.60
14Cl	495.18	38.69	38.45 and 38.66
	1279.98	100.00	99.50

In view of the fact that this salt is formed only in presence of an excess of antimony chloride, the above results may be considered as almost conclusive evidence in favor of the formula $Rb_5Sb_3Cl_{14}$. This salt is stable in comparatively dry air.

If the excess of antimony chloride added in the experiment last described be *very* great, a colorless salt crystallising in elongated, apparently orthorhombic, crystals is obtained, instead of the yellow salt. These crystals have brilliant faces when fresh, but on exposure to the air under ordinary conditions they soon become covered with an opaque white deposit, which probably consists of oxychloride of antimony, formed by surface decomposition of the salt. The compound was found to have a very simple formula, though the presence of so large an excess of antimony chloride at the time of its formation naturally makes the analytical results somewhat unsatisfactory. The salt cannot, of course, be recrystallised. As in the case of the salt just described, it was prepared for analysis merely by drying between filtering paper and then in a desiccator over calcium chloride.

0.4343 gram gave 0.2133 gram Sb_2S_3 (35.05 per cent. Sb), and 0.1489 gram RbCl (24.23 per cent. Rb).

0.4563 gram gave 0.2242 gram Sb_2S_3 (35.07 per cent. Sb), and 0.7495 gram AgCl (40.62 per cent. Cl).

	Calculated for $RbSbCl_4$.		Found.
Rb	85.2	24.60	24.23
Sb	119.6	34.54	35.05 and 35.07
4Cl	141.48	40.86	40.62
	346.28	100.00	99.90

The formula of this salt is therefore $RbSbCl_4$.

Summary.

The following is a list of the compounds of antimony chloride, with the chlorides of rubidium and cæsium obtained in this investigation. The formula of the first of the rubidium salts must be considered as somewhat doubtful.

$Cs_3Sb_2Cl_9$	$Rb_{23}Sb_{10}Cl_{53}$
	$Rb_5Sb_3Cl_{14}$
	$RbSbCl_4$

These formulas show that the elements in question have a marked tendency towards the formation of complex double chlorides. The most important conclusion, however, to be drawn from the present investigation is that neither the salt described by Godeffroy as $SbCl_3.6CsCl$ nor that described as $SbCl_3.6RbCl$ corresponds in composition to the formula proposed by him.

THEORETICAL.

There are now two well-established exceptions to the general law in regard to the composition of the double chlorides, namely, the salts $CuCl.2KCl$[1] and $CdCl_2.4KCl$[2]. It is to be noticed, however, that the structure of the salt $Rb_{23}Sb_{10}Cl_{53}$ cannot be represented on the same general system as that of the ordinary double chlorides, where two chlorine atoms are supposed to be analogous in function to one oxygen atom in the oxygen salts. This statement holds true even if the formula of this chloride be somewhat simpler than that here proposed. Hence this compound is perhaps quite as exceptional as the two simpler salts mentioned. In view of these facts the author offers the following formulas as suggestions of the possible structure of these compounds. Some of the bonds indicated are perhaps unnecessary. They are inserted merely for the sake of representing the chlorine atoms as invariably trivalent. The essential point is the conception that a group of three chlorine atoms can have three free valencies.

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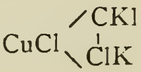
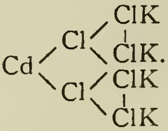
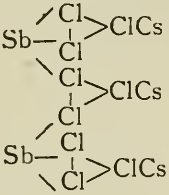
[1] Mitscherlich: Ann. chim. phys. [2] **73**, 384.

[2] C. v. Hauer: Wien. Akad. Ber. **15**, 23. These results have recently been confirmed by Dr. G. M. Richardson.





According to this method of writing, the salt $Cs_3Sb_2Cl_9$ could be represented by a symmetrical formula,



By doubling the formula it could, however, be written symmetrically according to the usual method, representing the chlorine atoms as always in pairs. By a combination of the two ideas—that a pair of chlorine atoms can have two free valencies, and that a group of three can have three free valencies—we can write a symmetrical formula for the salt $Rb_{23}Sb_{10}Cl_{53}$. It seems needless to give this structural formula here, as it covers a very large space. The formula of the salt $Rb_5Sb_3Cl_{14}$ can be written by representing all the chlorine atoms as united in pairs. As this is perhaps the simplest conception, an unnecessary departure from it would hardly be justifiable.

V.—On Some Double Halides of Bismuth.[1]

By C. Pliny Brigham.

Double halides of bismuth and potassium have been described as follows:

$BiCl_3.3KCl$, Arppe } Spec. Acad. d. 9 Oct. 1844, and Berzelius'
$BiCl_3.2KCl$, Arppe } Jahrsb. **25**, 279.
$BiCl_3.2KCl + 2H_2O$, Jacquelaine: Ann. chim. phys. **66**, 113.

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[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1891.

$$\left.\begin{array}{l}\mathrm{BiI_3.2KI + H_2O}\text{, Arppe}\\ \mathrm{BiI_3.4KI + HI}\text{ (?), Arppe}\end{array}\right\}\text{Spec. Acad. 5 Juni, 1844, and Berzelius' Jahrsb. }\mathbf{25}\text{, 284.}$$

$BiCl_3.2KBr + 1\frac{1}{2}H_2O$, Atkinson: J. Chem. Soc. 1883, 292.

Of these I have worked only with the chlorides.

There are recorded a number of other double halides of bismuth which are here tabulated.

$$\left.\begin{array}{l}\mathrm{BiCl_3.2NaCl + 3H_2O}\text{, Jacquelaine:}\\ \mathrm{BiCl_3.NH_4Cl}\text{, Jacquelaine:}\end{array}\right\}\text{Ann. chim. phys. }\mathbf{66}\text{, 113.}$$

$$\left.\begin{array}{l}\mathrm{BiCl_3.2NH_4Cl}\text{, Deherain:}\\ \mathrm{BiCl_3.3NH_4Cl}\text{, Deherain:}\end{array}\right\}\text{Compt. rend. }\mathbf{54}\text{, 724.}$$

$$\left.\begin{array}{l}\mathrm{BiBr_3.3NH_4Cl + H_2O}\text{, Muir:}\\ \mathrm{BiBr_3.2NH_4Cl + 3H_2O}\text{, Muir:}\end{array}\right\}\text{J. Chem. Soc. 1876, 148.}$$

$BiBr_3.2NH_4Cl + 5H_2O$, Nicklès: J. Chem. Soc. 1876, 148.

$2BiBr_3.5NH_4Cl + H_2O$, Muir: J. Chem. Soc. 1877, 28.

Of other double salts of bismuth there are two of the composition:

$$\left.\begin{array}{l}\mathrm{3K_2SO_4.Bi_2(SO_4)_3,}\\ \mathrm{2K_2SO_4.BiO(SO_4)_2,}\end{array}\right\}\text{Berzelius' Jahrsb. }\mathbf{25}\text{, 286.}$$

I speak of these simply because in a method of analysis employed for the determination of chlorine in the double chloride $BiCl_3.2KCl + 2H_2O$, I obtained a salt, a double sulphate, differing in composition from either of the above, and mention of which I have been unable to find in the literature.

Godeffroy[1] describes the salts $BiCl_3.6RbCl$ and $BiCl_3.6CsCl$, which are plainly marked exceptions to Professor Remsen's law. With these facts at hand, the following work on the double salts of bismuth chloride with the chlorides of rubidium and cæsium was undertaken to determine whether or not these compounds really exist.

Method of Analysis.

Although Godeffroy in his article gives the results of complete analyses of the different salts described therein, he fails to give the method employed, which would indicate, to say the least, that they are simple; but the analysis of the double chlorides of bismuth and the alkalies presents many difficulties, a few of which I will mention. Freshly prepared ammonium sulphide was added to the double salt in water; the sulphide of bismuth thus formed was filtered off on a washed filter, washed with water containing a little hydrogen sulphide, dried in an air-bath at 90°, scraped

[1] Berichte **8**, 9, und Zeitschrift des allgemeinen österreichischen Apotheker-Vereins.

into a weighed porcelain crucible, and, together with the ash from the filter, was treated with a few drops of pure concentrated nitric acid, the lid to the crucible being so placed as to avoid loss by spattering. The contents of the crucible were evaporated to dryness over a water-bath, heated to constant weight over a Bunsen burner, and finally over a blast-lamp, the bismuth oxide thus obtained melting without loss in weight. Before precipitating the chlorine in the filtrate from bismuth sulphide, it is first necessary to remove the excess of ammonium sulphide; to accomplish this, cadmium nitrate, free from arsenic, was added, and the cadmium sulphide formed filtered off. Copper sulphate was tried, but was found not to answer, as the sulphide of copper is partially soluble in ammonium sulphide. To the filtrate from cadmium sulphide was added a little nitric acid and silver nitrate, and the chlorine determined as silver chloride. The results obtained in this way were always 4 or 5 per cent. low; this error arises from the fact that when ammonium sulphide is used to precipitate the bismuth, some oxychloride comes down with the sulphide.

It was hoped that by dissolving the double salt in a little nitric acid and then adding a sulphide this trouble could be overcome, but if this is done a large amount of sulphur is thrown out with the bismuth sulphide, which seriously interferes with the determinations of bismuth.

After several months' work the following method was found to give satisfactory results.

A weighed portion of the salt, not more than 0.2 gram, is treated with about 20 cc. water containing 1 cc. pure concentrated hydrochloric acid, and heated nearly to boiling: there should be enough acid present to prevent the formation of any basic bismuth salts. Hydrogen sulphide is then passed in until the supernatant liquid becomes clear. The bismuth sulphide thus formed is filtered off on a quantitative filter, and washed with water containing a little hydrogen sulphide, dried, transferred to a weighed porcelain crucible, treated with a few drops of pure concentrated nitric acid, evaporated to dryness, and heated to a constant weight with a Bunsen burner, and finally over a blast-lamp. Bismuth is calculated from the oxide thus obtained.

Besides determining bismuth as the oxide, I also determined it directly from the sulphide by filtering this through a Gooch crucible and drying it at 100° to constant weight. Both of these methods give good results.

To determine the alkali, the filtrate is evaporated to dryness, dissolved again in a little water, filtered into a weighed platinum crucible, evaporated to dryness on a water-bath, and then heated for two hours at 235° in an air-bath, and when cool weighed; in the case of cæsium it was heated only to about 170°. The crucible is then heated for a few seconds only over a Bunsen burner to a dull red heat and again weighed; the loss here is generally less than 0.0004 gram. To make the results more accurate, the alkali thus determined as the chloride must be dissolved in a little hot water and filtered, the filter burned and weighed; thus any insoluble matter present, such as silicates, from the glass vessel used in evaporation can be detected and their weight subtracted from the weight of the alkali obtained. This method gives good results.

To determine chlorine a second sample of the salt is dissolved in about 30 cc. of water, containing several cubic centimeters of pure concentrated nitric acid, free from chlorine, and heated almost to boiling, when about 15 cc. more of nitric acid is added; this large excess of acid is necessary to prevent the formation of any basic bismuth salts; the chlorine is then precipitated by a not too weak solution of silver nitrate; the silver chloride is filtered off in a Gooch crucible, first washed with water containing nitric acid, and finally with water alone. The results for chlorine obtained in this way are entirely satisfactory.

Di-potassium Chloro-bismuthite,
$K_2BiCl_5 + 2H_2O$, ($BiCl_3.2KCl + 2H_2O$).

Arppe describes a salt K_3BiCl_6, ($BiCl_3.3KCl$), and states that when three molecular weights of bismuth oxide are dissolved in hydrochloric acid and two molecular weights of potassium chloride are added, on evaporation rhombic crystals separate out, which on analysis can be shown to have the composition K_3BiCl_6.

Following these directions closely I obtained beautiful four-sided crystals with two opposite angles cut off, thus presenting a six-sided appearance; the analysis of this salt showed it to have the composition $BiCl_3.2KCl + 2H_2O$.

The results obtained are here given:

0.1421 gram salt gave 0.0659 gram Bi_2O_3 = 0.0591 gram Bi.
0.1472 gram salt gave 0.2115 gram AgCl = 0.0523 gram Cl.
0.1419 gram salt gave 0.0417 gram KCl = 0.0219 gram K.
0.1025 gram salt lost 0.0074 gram H_2O.

	Calculated for $BiCl_3.2KCl + 2H_2O$.	Found.
Bi	41.63	41.57
K	15.66	15.49
Cl	35.48	35.51
H_2O	7.20	7.18

This salt is stable in the air; it does not lose its water of crystallisation in a desiccator, but when heated to 100° becomes anhydrous. It dissolves in moderately concentrated hydrochloric acid, and can be recrystallised from the same without any change in composition. Its crystallising power is very great.

All attempts to get the salt with three molecules of potassium chloride were fruitless. Bismuth oxide and potassium chloride were mixed in the exact proportions, one molecule of the former to six of the latter, yet the only salt obtained was $K_2BiCl_5 + 2H_2O$. Again a large excess of potassium chloride was used, and under these conditions potassium chloride crystallised out first and then the double salt with two molecules of the alkali chloride. Hence I feel justified in asserting that no salt of the formula K_3BiCl_6 exists.

Although no description of a double salt of bismuth and potassium chlorides containing less than two atoms of potassium to one of bismuth could be found, an investigation on this point was made, when a salt of the composition $KBiCl_4 + H_2O$, ($BiCl_3.KCl + H_2O$) was obtained.

Mono-potassium Chloro-bismuthite,
$KBiCl_4 + H_2O$, ($BiCl_3.KCl + H_2O$).

When bismuth oxide and potassium chloride are dissolved in hydrochloric acid in the proportion of 2½ molecules of the former to 2 of the latter, and the solution evaporated to a syrupy consistency, beautiful fiber-like needles radiating from centres crystallise out. If the solution be not sufficiently concentrated by evaporation, the salt $K_2BiCl_5 + 2H_2O$ invariably crystallises out. The analysis of this salt, dried first by means of a porous plate and then between filter-papers, gave these results:

I. 0.4109 gram salt gave 0.2338 gram Bi_2O_3 = 0.2096 gram Bi.
II. 0.1758 gram salt gave 0.1005 gram Bi_2O_3 = 0.0901 gram Bi.
III. 0.1910 gram salt gave 0.1095 gram Bi_2O_3 = 0.0982 gram Bi.

I. 0.1910 gram salt gave 0.0363 gram KCl = 0.0190 gram K.
II. 0.1753 gram salt gave 0.0324 gram KCl = 0.017 gram K.

I. 0.1752 gram salt gave 0.2503 gram $AgCl = 0.0619$ gram Cl.
II. 0.2082 gram salt gave 0.2976 gram $AgCl = 0.0736$ gram Cl.

I. 0.4109 gram salt lost 0.019 gram H_2O.
II. 0.45405 gram salt lost 0.0167 gram H_2O.

	Calculated for $BiCl_3.KCl + H_2O$.	Found. I.	II.	III.
Bi	51.11	51.01	51.25	51.39
K	9.62	9.96	9.66	...
Cl	34.85	35.31	35.32	...
H_2O	4.43	4.52	...	3.67

The sample of salt used in analysis III was made from a solution containing a very large excess of bismuth chloride, which readily accounts for the high percentage of bismuth and the low percentage of water found. This salt is stable in the air; it cannot be recrystallised except from a strong solution of bismuth chloride, from which the salt cannot be completely freed. When crystallised from hydrochloric acid it goes over into $K_2BiCl_5 + 2H_2O$, which appears to be the most stable of the double chlorides of bismuth and potassium. This salt, $KBiCl_4 + H_2O$, when placed in a desiccator over chloride of calcium, loses one-half of its water, while the remainder cannot be driven off below 100°.

Weight of the tube + salt (dried on a porous plate),	8.8701 grams.	
“ “ “ empty,	8.4592	
“ “ salt,	0.4109	
“ “ tube + salt dried to constant weight in a desiccator,	8.8608	
“ “ tube + salt heated to constant weight at 105°,	8.8515	
Loss in weight of salt dried at 105°,	0.0186	
“ “ “ “ in a desiccator,	0.0093	
Percentage of water lost by drying in a desiccator,		2.26
Total percentage of water lost when the salt is heated to constant weight at 105°,		4.52

Thus it appears that in the salt dried over calcium chloride, there is ½ a molecule of water of crystallisation.

A sample of this salt was heated to 140°, but the loss in weight indicated the presence of but 1 molecule of water. When a higher temperature was tried the salt underwent a slight decomposition.

Potassium-bismuth Alum, $KBi(SO_4)_2$, $[K_2SO_4.Bi_2(SO_4)_3]$.

In trying to overcome the difficulties of analysing the double chloride for chlorine, a method was tried which unexpectedly yielded a salt of the composition $KBi(SO_4)_2$.

A weighed quantity of the double chloride of bismuth and potassium was placed in an Erlenmeyer flask and treated with concentrated sulphuric acid, the hydrochloric acid set free being conducted into a dilute solution of sodium hydroxide. After heating the contents of the flask for several hours, fine needle-shaped crystals appeared on cooling. On the addition of water they dissolved, and by evaporation of the solution they were again deposited in the needle form, as well as in beautiful glistening plates.

The analysis of these crystals shows them to have the composition $K_2SO_4.Bi_2(SO_4)_3$, or $KBi(SO_4)_2$, analogous to ordinary alum, $KAl(SO_4)_2 + 12H_2O$. As might be expected, this salt has no water of crystallisation, being formed in concentrated sulphuric acid. These are the results obtained:

I. 0.3478 gram salt gave 0.1841 gram $Bi_2O_3 = 0.1650$ gram Bi.
II. 0.2081 gram salt gave 0.1109 gram $Bi_2O_3 = 0.0994$ gram Bi.
I. 0.2081 gram salt gave 0.0416 gram $K_2SO_4 = 0.0187$ gram K.
II. 0.2388 gram salt gave 0.0477 gram $K_2SO_4 = 0.0215$ gram K.
I. 0.3478 gram salt gave 0.3672 gram $BaSO_4 = 0.1511$ gram SO_4.
II. 0.1248 gram salt gave 0.1337 gram $BaSO_4 = 0.0550$ gram SO_4.

	Calculated for $KBi(SO_4)_2$.	Found.	
		I.	II.
Bi	47.36	47.44	47.77
K	8.91	8.99	8.98
SO_4	43.72	43 46	44.10

The method of analysis is as follows: Dissolve a weighed quantity of the salt in water and hydrochloric acid, add barium chloride to precipitate all the sulphuric acid as barium sulphate: there must be enough hydrochloric acid present to prevent the formation of any basic bismuth salts. Filter off into a Gooch crucible the barium sulphate, wash first with dilute hydrochloric acid, and finally with water; dry and weigh.

The bismuth in the filtrate can be determined, if too much acid be not present; or a new sample dissolved in hydrochloric acid and water may be taken: in this case the determination is exactly the same as in the case of the double chlorides.

To determine the potassium, a third sample is dissolved as before, hydrogen sulphide passed in to precipitate the bismuth, which is filtered off, and the filtrate evaporated to dryness, redissolved, filtered into a weighed platinum dish and again evaporated to dryness. 3 to 5 drops of sulphuric acid is then added and the substance heated to constant weight over a free flame, the acid salt first formed being transformed finally into potassium sulphate, from the weight of which the potassium is calculated.

This salt possesses the remarkable property of being quite insoluble in cold water; on boiling, however, it is decomposed into a bismuthyl sulphate of the composition $(BiO)_2SO_4 + 2H_2O$.

A quantity of the salt $KBi(SO_4)_2$ was boiled in water and the insoluble part filtered off and dried on a porous plate, and analysed with the following results:

0.0896 gram salt gave 0.0717 gram $Bi_2O_3 = 0.0643$ gram Bi.

0.0896 gram salt gave 0.0357 gram $BaSO_4 = 0.0147$ gram SO_4.

	Calculated for $(BiO)_2SO_4 + 2H_2O$.	Found.
Bi	71.72	71.74
SO_4	16.55	16.39

In the filtrate potassium and sulphuric acid were found, hence the decomposition may be expressed thus:

$$2BiK(SO_4)_2 + 2H_2O = (BiO)_2SO_4 + K_2SO_4 + 2H_2SO_4,$$
$$\text{or} = (BiO)_2SO_4 + 2KHSO_4 + H_2SO_4.$$

Potassium-antimony Alum.

By analogous methods of work I hoped to obtain a double sulphate of antimony and potassium, as well as one of arsenic and potassium, thus making more complete a series of double salts analogous to the well-known alums.

I first made the double chloride of antimony and potassium, then boiled it with concentrated sulphuric acid for eight hours: on cooling, well crystallised needles separated out. On the addition of water, instead of behaving like the corresponding bismuth compound, it immediately broke down into basic antimony sulphate. A second sample of the double chloride was heated for two days with concentrated sulphuric acid: on cooling the same crystalline mass appeared, and on the addition of water acted as before. A third sample was heated for eight hours with concentrated sulphuric acid, and instead of trying to recrystallise the mass, the excess of acid was poured off and the salt placed on a porous plate to dry: by this treatment the salt absorbed moisture from the air, and changed gradually into basic antimony sulphate. It was next placed in a vacuum over soda-lime and caustic potash. At the end of one month it was fairly dry, although the excess of acid had not entirely disappeared. An analysis was made which gave 17.9 per cent. antimony and 0.78 per cent. potassium, or a ratio between the atoms of antimony and potassium of 0.489 to 0.0669, instead of 1 to 1.

Further investigation of this salt was given up, as it was found impossible to get it pure enough for sharp analysis. The work done tends, however, to show the non-existence of a salt of the composition $KSb(SO_4)_2$ analogous to $KBi(SO_4)_2$. This is not surprising, since antimony is a much weaker base than bismuth and has greater acid properties; hence we can trace a gradation: in ordinary alum, $KAl(SO_4)_2$, we have great stability, especially toward water; with bismuth-potassium sulphate, we find a tendency to break down on boiling with water, while in the case of antimony no double salt, $KSb(SO_4)_2$, can be obtained. Arsenic having still greater acid properties will probably act like antimony and show no signs of forming a double sulphate. It would be interesting to see whether an analogous compound containing boron could be made.

Tri-rubidium Chloro-bismuthite, Rb_3BiCl_6,
$(BiCl_3.3RbCl)$.

The only work on the double chlorides of bismuth and rubidium was done by Godeffroy, who published his results in 1875. He describes and gives a complete analysis of the salt Rb_6BiCl_9, $(BiCl_3.6RbCl)$, which forms a marked exception to the law regarding the composition of the double halides. As many of the salts described by Godeffroy which have appeared as exceptions to the law, have by subsequent work been shown not to exist, it was deemed advisable carefully to investigate this double chloride, and determine first whether or not it has the composition Rb_6BiCl_9; secondly, whether by the further addition of bismuth or rubidium chloride a salt can be formed containing a greater or less percentage of bismuth similar to the salts obtained in the case of potassium. His description of the salt is briefly this:

By evaporation of a hydrochloric acid solution of bismuth chloride with rubidium chloride, beautiful crystals separate out. His analysis is as follows:

0.1535 gram salt gave 0.191 gram AgCl = 0.0473 gram Cl.
0.1535 gram salt gave 0.036 gram Bi_2O_3 = 0.03088[1] gram Bi.
0.423 gram salt gave 0.707 gram Rb_2PtCl_6 = 0.2077 gram Rb.

	Calculated for $BiCl_3.6RbCl$.	Found.
Bi	20.00	20.120
Cl	30.72	30.803
Rb	49.28	49.110

In order to give the best chance for the formation of this salt, rubidium chloride was dissolved in a little cold dilute hydrochloric acid, and drop by drop to this was added a hydrochloric acid solution of bismuth chloride, as the presence of a large excess of rubidium chloride should give the most favorable opportunity for the formation of a salt containing six atoms of rubidium, if formed at all. On the addition of the slightest quantity of bismuth chloride a voluminous crystalline precipitate was immediately formed, no evaporation being necessary. Godeffroy states that there is no precipitate formed when solutions of bismuth and rubidium chlorides are mixed. A small quantity of this precipitate was removed, dried on a porous plate, and analysed with the following results:

0.1884 gram salt gave 0.0644 gram Bi_2O_3 = 0.0577 gram Bi.
0.1427 gram salt gave 0.0761 gram RbCl = 0.0538 gram Rb.
0.1999 gram salt gave 0.2551 gram AgCl = 0.0631 gram Cl.

	Calculated for $BiCl_3.3RbCl$.	Found.
Bi	30.72	30.65
Rb	37.84	37.68
Cl	31.42	31.54

On heating a sample of this salt for two hours at 110° it lost in weight but slightly, giving only 0.2 per cent. loss, which was probably due to incomplete drying. Thus the analysis of this precipitate shows that it has the composition Rb_3BiCl_6, ($BiCl_3.3RbCl$), and not Rb_6BiCl_9, ($BiCl_3.6RbCl$).

Another portion of the precipitate was dissolved in moderately concentrated hydrochloric acid and the solution evaporated, when beautiful transparent crystals separate out, which, on the addition of concentrated hydrochloric acid, become opaque. These crystals are diamond-shaped, very regular in form, and similar to those of the potassium salt $K_2BiCl_5 + 2H_2O$, but without the truncations of the two opposite angles. The crystallising power of this salt is weak, consequently the crystals are of small size, but quite uniform. These crystals were dried on porous plates and then pressed between drying paper, and on analysis gave the following results:

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[1] A miscalculation; should be 0.032274 gram Bi.

I. 0.1552 gram salt gave 0.0536 gram Bi_2O_3 = 0.0480 gram Bi.
II. 0.2132 gram salt gave 0.0734 gram Bi_2O_3 = 0.0658 gram Bi.
I. 0.1835 gram salt gave 0.0985 gram RbCl = 0.0696 gram Rb.
II. 0.1609 gram salt gave 0.0860 gram RbCl = 0.0608 gram Rb.
I. 0.1349 gram salt gave 0.1777 gram AgCl = 0.0439 gram Cl.
II. 0.2093 gram salt gave 0.2670 gram AgCl = 0.0660 gram Cl.

	Calculated for $BiCl_3.3RbCl$.	Found. I.	II.
Bi	30.72	30.97	30.86
Rb	37.84	37.93	37.76
Cl	31.42	31.49	31.53

The recrystallised precipitate, when heated to 110° for two hours, lost but slightly in weight, showing that there is no water of crystallisation in the salt, the decrease being due to insufficient drying, a little hydrochloric acid probably being present.

This salt dissolves without decomposition in dilute hydrochloric acid, and, on evaporation of the solution, it always crystallises out in the same form. Water decomposes it with the formation of basic bismuth chloride and rubidium chloride.

Other attempts to obtain the salt of Godeffroy were made by using a cold concentrated solution of rubidium chloride and a cold dilute solution of bismuth chloride. Hot solutions also were used, but without success, the salt crystallising out always having the composition Rb_3BiCl_6.

A more complex Chloride of Rubidium and Bismuth,
$Rb_{23}Bi_{10}Cl_{53}$, ($10BiCl_3.23RbCl$) (?).

When bismuth oxide and rubidium chloride are mixed in the proportion of one molecular weight of the former to two of the latter, and the mixture dissolved in dilute hydrochloric acid and the solution evaporated, there separates out a salt crystallising in most varied forms resembling shapes of snow crystals, which, however, on standing, change and assume the form of hexagonal plates. These crystals are transparent, quite small, but very regular in habit. This salt was obtained in such small quantities that purification by crystallisation was impossible; in fact, when crystallised from hydrochloric acid it passes over into the compound Rb_3BiCl_6:

it can, however, be recrystallised from a solution of bismuth chloride.

The analysis of this salt did not give results sharp enough to lead to a definite formula. This is no doubt due to the impossibility of purifying it by repeated crystallisation. The following results were obtained:

I. 0.1563 gram salt gave 0.0603 gram Bi_2O_3=0.0541 gram Bi.
II. 0.2483 gram salt gave 0.0973 gram Bi_2O_3=0.0872 gram Bi.
I. 0.1563 gram salt gave 0.0719 gram RbCl=0.0508 gram Rb.
II. 0.2483 gram salt gave 0.1138 gram RbCl=0.0815 gram Rb.
I. 0.1525 gram salt gave 0.1956 gram AgCl=0 0484 gram Cl.
II. 0.1992 gram salt gave 0.2551 gram AgCl=0.0631 gram Cl.

	Calculated for $10BiCl_3.23RbCl$.	Found. I.	II.
Bi	35.11	34.58	35.17
Rb	33.17	32.50	32.83
Cl	31.72	31.74	31.66

From analysis I. the calculated ratio between the bismuth and rubidium atoms is 1 : 2.296, and from analysis II., 1 : 2.275, and the formula which would seem most probable in view of these results is $Rb_{23}Bi_{10}Cl_{53}$, or $10BiCl_3.23RbCl$.

Were it not for certain facts established by Mr. C. E. Saunders[1] the above formula would seem highly improbable. This gentleman, working on the double chlorides of antimony and rubidium, obtained a salt crystallising in the same form, the analysis of which gave a ratio between the antimony and rubidium atoms of 1 : 2.296.

Bismuth being so closely related to antimony, and the work on the double chloride of the latter with rubidium having shown the existence of a salt of the probable composition $10SbCl_3.23RbCl$, it is not surprising that a similar compound of bismuth should be formed. From the results actually obtained by me in the analysis of the salt above described, I think it highly probable that the composition of this salt corresponds to the formula $Rb_{23}Bi_{10}Cl_{53}$.

The salt $Rb_{23}Bi_{10}Cl_{53}$ dissolves to a clear solution in dilute hydrochloric acid, from which on partial evaporation there crystallises out the salt Rb_3BiCl_6, which is the form that these elements always assume under ordinary conditions. In water this salt decomposes with the formation of basic bismuth chloride.

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[1] See preceding article, p. 160.

Mono-rubidium Chloro-bismuthite,
$RbBiCl_4 + H_2O$, $(BiCl_3.RbCl + H_2O)$.

Besides the compounds Rb_3BiCl_6 $(BiCl_3.3RbCl)$, and $Rb_{23}Bi_{10}Cl_{53}$ $(10BiCl_3.23RbCl)$, another was obtained which in all probability corresponds to the mono-potassium chloro-bismuthite of the composition $RbBiCl_4 + H_2O$.

It was found that, when 2½ molecular weights of bismuth oxide were dissolved in concentrated hydrochloric acid, and 2 molecular weights of rubidium chloride were added and the solution evaporated to a syrupy consistency, after a time white hair-like crystals formed, and finally the contents of the vessel became almost solid. The beaker in which the salt was formed was turned on its side and the liquid allowed to drain off, after which the crystals were transferred to a porous plate and finally dried between filter-papers. If the evaporation of the solution be stopped before the liquid becomes sufficiently concentrated for the formation of these needle-like crystals, crystals of the compound $10BiCl_3.23RbCl$ always separate out, while, on the contrary, should the evaporation be carried beyond the point at which the hair-like crystals first form, these needles, although they are formed, do not appear separate, but seem to start from points and form themselves into a solid mass radiating from these points as centres.

The rubidium chloride used in this experiment was found on analysis to be slightly impure, containing probably a slight trace of cæsium.

0.2522 gram RbCl gave 0.2866 gram AgCl = 0.0708 gram Cl = 28.09 per cent. Theoretical per cent. of chlorine in RbCl = 29.34.

The conditions under which this double salt is formed, in a very concentrated solution of bismuth chloride, give little opportunity for the purification of the salts used. Were this salt formed in dilute acid solution, any impurity present in the rubidium chloride might be removed by the difference in solubility of the double salts produced; but being formed in such concentrated solutions, where bismuth chloride is present in such large excess, and where it appears as if all of both constituents present enter into combination, it is not surprising that, if cæsium is the impurity in the rubidium chloride, it would be carried along by both constituents and enter into combination.

This is probably the reason why the analyses of the salt do not correspond to any simple formula, although the similarity in the method of formation and in appearance to the potassium salt of the composition $KBiCl_4 + H_2O$ makes it appear probable that it has the composition $RbBiCl_4 + H_2O$.

The results of the analyses of three different samples are as follows:

Sample A.

I. 0.1275 gram salt gave 0.0622 gram $Bi_2O_3 = 0.0558$ gram Bi.
II. 0.1223 gram salt gave 0.0598 gram $Bi_2O_3 = 0.0536$ gram Bi.

Sample B.

I. 0.1315 gram salt gave 0.0743 gram $Bi_2S_3 = 0.0603$ gram Bi.
II. 0.1263 gram salt gave 0.0643 gram $Bi_2O_3 = 0.0576$ gram Bi.
III. 0.4108 gram salt gave 0.2315 gram $Bi_2S_3 = 0.1880$ gram Bi.

Sample C.

I. 0.2150 gram salt gave 0.1212 gram $Bi_2S_3 = 0.0984$ gram Bi.
II. 0.1666 gram salt gave 0.0940 gram $Bi_2S_3 = 0.0763$ gram Bi.

Sample A.

I. 0.1275 gram salt gave 0.0394 gram $RbCl = 0.0278$ gram Rb.
II. 0.1223 gram salt gave 0.0379 gram $RbCl = 0.0268$ gram Rb.

Sample B.

I. 0.1315 gram salt gave 0.0408 gram $RbCl = 0.0288$ gram Rb.
II. 0.1263 gram salt gave 0.0408 gram $RbCl = 0.0288$ gram Rb.

Sample C.

II. 0.1666 gram salt gave 0.0520 gram $RbCl = 0.0368$ gram Rb.

Sample A.

I. 0.1204 gram salt gave 0.1564 gram $AgCl = 0.0387$ gram Cl.
II. 0.1829 gram salt gave 0.2379 gram $AgCl = 0.0588$ gram Cl.

Sample B.

I. 0.1203 gram salt gave 0.1562 gram $AgCl = 0.0386$ gram Cl.
II. 0.1739 gram salt gave 0.2261 gram $AgCl = 0.0559$ gram Cl.

Sample C.

I. 0.2189 gram salt gave 0.2848 gram $AgCl = 0.0704$ gram Cl.
II. 0.2578 gram salt gave 0.3350 gram $AgCl = 0.0828$ gram Cl.

Sample A.

I. 0.4347 gram salt lost 0.011 gram H_2O, heated for 2 hours at 105°.

Sample B.

I. 0.4151 gram salt lost 0.0043 gram H_2O, heated for 2 hours at 105°.

Sample C.

I. 0.4085 gram salt lost 0.0067 gram H_2O, heated for 2 hours at 105°.

II. 0.1957 gram salt lost 0.00295 gram H_2O, heated for 2 hours at 105°.

Sample A.

	Calculated for		Found.	
	$RbBiCl_4 + H_2O$.	$RbBiCl_4$.	I.	II.
Bi	45.89	47.77	43.73	43.83
Rb	18.84	19.62	21.83	21.89
Cl	31.29	32.58	32.10	32.17
H_2O	3.97	...	2.53	...

Sample B.

	Calculated for		Found.		
	$RbBiCl_4 + H_2O$.	RbBiCl.	I.	II.	III.
Bi	45.89	47.77	45.89	45.64	45.77
Rb	18.84	19.62	21.29	22.54	...
Cl	31.29	32.58	32.09	32.14	...
H_2O	3.97	...	1.03	...	...

Sample C.

	Calculated for		Found.	
	$RbBiCl_4 + H_2O$.	$RbBiCl_4$.	I.	II.
Bi	45.89	47.77	45.78	45.82
Rb	18.84	19.62	...	22.11
Cl	31.29	32.58	32.16	32.11
H_2O	3.97	...	1.64	1.50

The bismuth in analyses I. and III., sample *B*, and I. and II., sample *C*, was determined as the sulphide, while that in I. and II., sample *A*, and II., sample *B*, was calculated from the oxide.

It will be seen on comparing the results calculated for $RbBiCl_4 + H_2O$ with the percentages found, that while there is a discrepancy in the case of rubidium and water, the percentages for bismuth and chlorine are close.

This salt is decomposed by water, but yields a clear solution when treated with dilute hydrochloric acid, from which on slight evaporation the salt $BiCl_3.3RbCl$ separates.

All efforts to obtain salts composed of bismuth and rubidium chlorides other than have here been described have proved fruitless. From these facts it appears to follow that the salt $BiCl_3.6RbCl$, described by Godeffroy, does not exist.

Cæsium-bismuth Chlorides.

As with rubidium, so with cæsium, Godeffroy describes a salt of the composition $BiCl_3.6CsCl$, and to determine whether such a compound exists the following work was undertaken. On analysis the cæsium chloride obtained from one of the best known dealers was found to be very impure, containing most probably rubidium and potassium. Before beginning the investigation of the double chloride it was therefore necessary to purify this salt. The method[1] employed depends on the difference in solubility of the double salts of antimony-rubidium chloride and antimony-cæsium chloride, the former being soluble in concentrated hydrochloric acid, the latter not.

The cæsium chloride was dissolved in moderately concentrated hydrochloric acid, and a solution of antimony chloride in hydrochloric acid added, until it ceased to give a precipitate. The solution was allowed to stand until clear, when the supernatant liquid was poured off. Concentrated hydrochloric acid was added to the precipitate, in which case any rubidium-antimony chloride present would dissolve. This liquid was poured off when the precipitate remaining should contain only cæsium-antimony chloride. This was dissolved in hot concentrated hydrochloric acid, and hydrogen sulphide passed in for a *long* time, as the large quantity of acid used to dissolve the salt prevents the complete precipitation of the antimony at once. The antimony sulphide was filtered off, and the filtrate containing the cæsium chloride was evaporated to dryness in a *platinum* dish; if a glass or porcelain vessel is used, some alkali from the glass will be dissolved; to drive off the last trace of hydrochloric acid, it was heated to 130° in an air-bath.

The cæsium chloride thus treated was found to be much purer than that with which I started; yet a second purification seemed advisable, the result of which gave me a small quantity of the salt, which on analysis gave these results:

0.1711 gram CsCl gave 0.147 gram AgCl $=$ 0.0363 gram Cl $=$ 21.23 per cent. Theoretical percentage of chlorine in cæsium chloride $=$ 21.05.

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[1] Ann. Chem. (Liebig) **181**, 183.

This is probably as pure as cæsium chloride can be obtained by this method; the quantity of the salt would not permit a third purification.

Godeffroy[1] in his description of the salt $BiCl_3.6CsCl$ says that, by mixing solutions of bismuth and cæsium chlorides in hydrochloric acid, he obtained a precipitate which is difficultly soluble, and gave these results:

0.900 gram salt gave 0.861 gram $AgCl = 0.213$ gram Cl.
0.900 gram salt gave 0.154 gram $Bi_2O_3 = 0.138$ gram Bi.
0.515 gram salt gave 0.788 gram $Cs_2PtCl_6 = 0.3095$ gram Cs.

	Calculated for $BiCl_3.6CsCl$.	Found.
Cl	24.10	23.67
Bi	15.68	15.37
Cs	60.22	60.09

Following these directions, to a saturated solution of cæsium chloride in dilute hydrochloric acid a solution of bismuth chloride was added drop by drop, when a voluminous precipitate, difficultly soluble, was formed. A close examination of this precipitate showed the presence of two distinct kinds of crystals. However, to follow Godeffroy's direction and obtain his salt this precipitate as obtained was analysed. A sample dried on a porous plate and finally between filter-papers gave these results:

I. 0.171 gram salt gave 0.0701 gram $Bi_2S_3 = 0.0569$ gram Bi.
II. 0.1881 gram salt gave 0.0782 gram $Bi_2S_3 = 0.0635$ gram Bi.
I. 0.171 gram salt gave 0.0862 gram $CsCl = 0.0681$ gram Cs.
II. 0.1881 gram salt gave 0.0947 gram $CsCl = 0.0748$ gram Cs.
I. 0.1534 gram salt gave 0.1693 gram $AgCl = 0.0418$ gram Cl.
II. 0.1507 gram salt gave 0.1671 gram $AgCl = 0.0413$ gram Cl.

	Calculated for		Found.	
	$BiCl_3.2CsCl$.	$BiCl_3.6CsCl$.	I.	II.
Bi	31.93	15.68	33.29	33.76
Cs	40.84	60.22	39.79	39.74
Cl	27.22	24.10	27.28	27.41

These results show that the precipitate is most probably a mixture, as it corresponds to no simple salt, but has a composition somewhat near $BiCl_3.2CsCl$.

The precipitate dissolves easily in warm dilute hydrochloric acid, one of the constituents apparently with more ease than the other, so that it is quite an easy matter to separate and obtain them both in pure condition by recrystallisation. On evaporation of a solution of the precipitate in hydrochloric acid, the more compact-looking crystals which settled to the bottom of the precipitate formed yellowish, elongated pyramids; while the others, which are the more easily soluble, assume a flaky appearance. These are white and transparent.

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[1] Zeitschrift des allgemeinen österreichischen Apotheker-Vereins.

After separation, each lot was recrystallised twice from dilute hydrochloric acid, and although but a small quantity of each was obtained, they appeared quite pure and gave excellent results on analysis.

Salt of the Composition $Cs_3Bi_2Cl_9$, ($2BiCl_3.3CsCl$).

That part of the precipitate formed by mixing solutions of cæsium and bismuth chlorides in hydrochloric acid, which on recrystallisation forms elongated pyramids, yellow in color, has the composition $Cs_3Bi_2Cl_9$, as shown by the following analytical results:

0.1587 gram salt gave 0.072 gram Bi_2S_3 = 0.0585 gram Bi.
0.1587 gram salt gave 0.0708 gram CsCl = 0.0559 gram Cs.
0.1390 gram salt gave 0.1586 gram AgCl = 0.0392 gram Cl.

	Calculated for $2BiCl_3.3CsCl$.	Found.
Bi	36.68	36.84
Cs	35.18	35.22
Cl	28.13	28.20

This salt, on treatment with water, decomposes with the formation of oxychloride of bismuth and cæsium chloride; in cold dilute hydrochloric acid it is difficultly soluble, but dissolves rapidly when warmed. With the formation of this salt, the similarity between the elements bismuth and antimony is again shown, as the chloride of the latter with cæsium chloride only forms a salt of the composition $Cs_3Sb_2Cl_9$.

Tri-cæsium Chloro-bismuthite, Cs_3BiCl_6, ($BiCl_3.3CsCl$).

That part of the precipitate which crystallises in thin transparent plates has the composition Cs_3BiCl_6.

The results obtained on analysis of this salt are as follows:

I. 0.1189 gram salt gave 0.0376 gram Bi_2S_3 = 0.0305 gram Bi.
II. 0.1730 gram salt gave 0.0544 gram Bi_2S_3 = 0.0442 gram Bi.
II. 0.1730 gram salt gave 0.1063 gram CsCl = 0.0829 gram Cs.
I. 0.0817 gram salt gave 0.0860 gram AgCl = 0.0313 gram Cl.

	Calculated for $BiCl_3.3CsCl$.	Found. I.	Found. II.
Bi	25.37	25.68	25.53
Cs	48.67	...	48.51
Cl	25.95	26.08	...

Through an accident the determination of cæsium in sample I. was lost.

The behavior of this salt is much like that of the composition $Cs_3Bi_2Cl_9$. It is difficultly soluble in cold dilute hydrochloric acid, but when warmed dissolves easily.

In the case of the double chlorides of rubidium and cæsium with bismuth, it was so difficult to obtain the compounds well crystallised that an investigation of their crystallographic properties was not undertaken.

Conclusion.

The principal results of this investigation are these:

I. Of the three double chloro-bismuthites of potassium only the one described by Jacquelaine, ($BiCl_3.2KCl + 2H_2O$),[1] exists, while one of the composition ($BiCl_3.KCl + H_2O$), not described in the literature, can be formed under certain conditions.

II. No salt of the composition Rb_6BiCl_9 exists, but from the chlorides of bismuth and rubidium the following salts can be formed: Rb_3BiCl_6, $Rb_{23}Bi_{10}Cl_{53}$, $RbBiCl_4 + H_2O$.

III. The salt to which Godeffroy ascribes the composition $BiCl_3.6CsCl$ is a mixture of the two salts Cs_3BiCl_6 ($BiCl_3.3CsCl$) and $Cs_3Bi_2Cl_9$ ($2BiCl_3.3CsCl$).

IV. As the atomic weight of the alkali in combination with bismuth increases, the amount of water of crystallisation decreases thus: $BiCl_3.2NaCl + 3H_2O$; $BiCl_3.2KCl + 2H_2O$; $BiCl_3RbCl + H_2O$; $BiCl_3.3CsCl$.

VI.—EXPERIMENTS WITH MERCUROUS HYPOCHLORSULPHITE.

BY J. E. GILPIN.

In connection with the work on the double halides that has been carried on in this laboratory for some time past, it was considered important to determine the molecular weight of one of these compounds by the aid of the specific gravity of its vapor. Capitaine[2] has described a compound of the formula $SCl_2.Hg_2Cl_2$ to which he gives the name mercurous hyposulphochloride (*chloride hyposulfureux*). According to the discoverer, this compound is volatile without decomposition. It can be made in two ways: (1) either by subliming a mixture of mercuric chloride and sulphur, in which the product appears as a coating of fine yellow needles, which are removed from time to time as they are formed; or (2) by letting a mixture of mercurous chloride and sulphur chloride stand together in the dark for some time, and, after the excess of sulphur chloride has been distilled off, subliming the residue as in the first method.

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[1] Ann. chim. phys. **66**, 113.

[2] J. prakt. Chem. **18**, 422.

In both cases the product has to be purified by sublimation. The product is crystalline, but cannot be recrystallised from solution, as solvents decompose it. During the investigation it was found that the substance does not act as Capitaine stated, but is decomposed. On resubliming the pure material partial decomposition took place, and when it was heated in a test-tube in a sulphuric-acid bath, decomposition began at about 80°, and if heated for some time to 180°, mercuric chloride was found coating the cool part of the tube while the sulphur remained at the bottom. The specimen made from mercuric chloride and sulphur and twice resublimed, gave on analysis:

0.4681 gram substance gave 0.0281 gram sulphur = 5.57 per cent. S.

0.4681 gram substance gave 0.3781 gram mercuric sulphide = 69.62 per cent. Hg.

0.4681 gram substance gave 0.4681 gram silver chloride = 24.72 per cent. Cl.

The calculated percentages for $SCl_2.Hg_2Cl_2$ are S = 5.58; Hg = 69.73; Cl = 24.68.

The specimen made from mercurous chloride and sulphur chloride gave the following results:

0.3893 gram substance gave 0.022 gram sulphur = 5.65 per cent. S.

0.3893 gram substance gave 0.3144 gram mercuric sulphide = 69.61 per cent. Hg.

0.3893 gram substance gave 0.3917 gram silver chloride = 24.87 per cent. Cl.

When this pure substance was sublimed again it was partly decomposed. Mercuric chloride remained at the bottom; but the upper part carefully removed gave the following analysis, showing that although it was partly decomposed, yet some of the original substance remained:

0.5113 gram substance gave 0.0258 gram sulphur = 5.04 per cent. S.

0.5113 gram substance gave 0.4135 gram mercuric sulphide = 69.71 Hg.

0.5113 gram substance gave 0.5086 gram silver chloride = 24.58 per cent. Cl.

After another sublimation of the last product the results showed that there was some free sulphur present, as the amounts were for sulphur 6.15 per cent., for mercury 68.55 per cent., and for chlorine 24.10 per cent.

This proof and the observations made when the substance is heated in a test-tube clearly establish the fact that decomposition takes place when it is heated to volatilise it.

The sulphur in the compound is in a very peculiar and sensitive condition. An attempt was made to add more chlorine to the compound in the hope of getting such a compound as $SCl_4.Hg_2Cl_2$; but it was found that when dry chlorine gas is passed over the substance at the ordinary temperature, all the sulphur is removed and passes off as sulphur chloride, leaving mercuric chloride behind in a perfectly pure state.

On account of the sensitive nature of the sulphur it was considered possible that this sulphur might act much more readily than free sulphur. Its action was tried on several amides, diphenyl-amine, aniline, and *p*-toluidine. Reactions took place easily in each case, but the mercuric chloride entered into the reaction, and compounds were formed whose true nature could not easily be determined. In the case of diphenyl-amine the reaction took place on heating to 80°; with aniline a reaction accompanied by a marked evolution of heat took place on stirring the substances together with a glass rod; and in the case of *p*-toluidine it was necessary to heat to 150°. The products were purified to remove any excess of the original substances, then dried and powdered. It was impossible to tell when the substances were pure; but the compound with *p*-toluidine was the easiest to purify on account of the solubility of the impurities. Diphenyl-amine gave a brown powder, aniline a blue one, and *p*-toluidine a black one. In each case the amides were treated with sulphur alone, and also with mercuric chloride, but the action did not take place unless both were present. The analyses showed the presence of sulphur, chlorine and mercury, and according to the results the compound is a mixture, or very complicated. The results agree nearly with a formula like $(C_6H_4.CH_3.NH_2)_2S_5Cl_5Hg_7$. Further experiments in this line will be undertaken as soon as possible.

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THE COLORS AND ABSORPTION-SPECTRA OF THIN METALLIC FILMS AND OF INCANDESCENT VAPORS OF THE METALS; WITH SOME OBSERVATIONS ON ELECTRICAL VOLATILITY.

BY WILLIAM L. DUDLEY.

Several years ago the writer began to investigate methods for obtaining metals in thin films, with a view to the study of the relations existing between their color by transmitted light and that emitted by their incandescent vapors; also to the study of their absorption-spectra. A number of methods were resorted to, for instance:

1. Volatilisation by boiling and condensation on glass;

2. Electro-deposition and removal of the "base" on which the metal is deposited by a suitable solvent;

3. Reduction of a salt which had been spread in a thin and uniform layer on the surface of a transparent base;

4. Volatilisation by the electric arc between terminals of the metal enclosed in a glass tube filled with an inert atmosphere; and

5. Volatilisation by the condensed electric spark under similar conditions.

Each method had its value in particular cases, but no one method seemed to be capable of universal application, although the last mentioned was generally applicable. I will describe briefly the various methods employed.

(1). Volatilisation by boiling was resorted to in dealing with potassium, sodium and lithium. Potassium, which had been freed from all mechanical impurities and hydrocarbons, was introduced into a glass tube filled with an atmosphere of hydrogen or nitrogen which was highly attenuated by a pump, and sealed. The portion of the tube in which lay the globule of metal was gradually heated over a Bunsen burner until the potassium boiled, when the tube was immediately withdrawn from the flame. The vapor of the potassium condensed in a thin film on the cooler portions of the tube, and exhibited in the thinnest parts colors by transmitted light ranging from violet to blue as the thickness increased, while by reflected light the film had the usual silvery metallic lustre of potassium. The film is not permanent. The brilliant colors gradually fade, until after some days they have completely disappeared, owing to the thin layer slowly drawing itself together into minute globules which to the unaided eye give to the whole surface a frosted appearance. By again heating the metal to boiling as before a new film can be produced.

Sodium and lithium were treated in the same manner as potassium. Sodium, however, gave a yellow-brown film, which was due to its action on the glass; the color was at first ascribed to the reduction of silica, but when lithium was treated in the same way the glass was also attacked, the color of the film being deep red-brown. The glass was permanently colored in each case, the metals having combined chemically with it, as one would naturally expect. The color conveyed by each was, however, a source of surprise, since it approached more or less closely, even under these circumstances, to that of its incandescent vapor. It may be accounted for in the same way as is gold "ruby" glass, *i. e.* is due to the presence of finely divided metal distributed through the glass. If thin gold leaf, which exhibits a fine green color by transmitted light, be spread out on a sheet of glass and heated to 316° or over, the color becomes red, and if the temperature has not been so high as to incorporate the gold with the glass, the green color may be restored by simply burnishing the surface.[1] The ruby color of the glass is held to be due to the gold in a finely divided state, and the colors given to glass by sodium and lithium may be due to the same cause. Many kinds of glass were employed—all, of course, without lead in their composition—and the effect was always the same.

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[1] Faraday, Phil. Trans. 1857, 145; also, his Experimental Researches in Chemistry and Physics.

(2). Electro-deposition is of limited application; gold films may, however, be readily produced, owing to the ease with which this metal is deposited; its resistance, too, to the action of acids making the separation of the film from the metal upon which it is deposited a simple matter.[1] A difficulty is encountered in this method in efforts to obtain films of proper thickness; this is, however, largely obviated by a method employed by Kundt,[2] in which he obtains a wedge-shaped film by placing the cathode horizontal in the bath and the anode very near, and perpendicular to, the surface of the cathode. Thus the film tapers out in a very thin edge. Arsenic deposited on glass by decomposing arsine may prove a good surface upon which to make the deposits, as it could easily be dissolved off of the film by sodium hypochlorite or some other suitable solvent. I have never tried it, however, as I found that other methods served my purpose in most instances.

(3). The reduction of a thin film of the metallic salt was found unsatisfactory for various reasons, and was not employed, although films of platinum could be obtained quite easily, giving a purple color by transmitted light.

(4). The electric arc between terminals of the metal to be volatilised proved successful in a few cases. The terminals were inserted into a glass tube filled with an inert atmosphere, and brought in contact for an instant. The metal was suddenly vaporised and thrown upon the glass, but was usually granular or powdery, of a black or brown color, altogether unsatisfactory, owing to its discontinuous character.

(5). The condensed spark between two points of the metal enclosed in a glass tube, exhausted, or filled with an inert atmosphere highly attenuated, serves well in many cases. For descriptions of this method in detail I refer to papers by Wright,[3] Hartley[4] and Crookes.[5] Hartley, however, volatilised the metals in the air, and consequently only a few of the films were metallic. The facility with which metals volatilise by this method varies very much:

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[1] Outerbridge, Paper by Eggleston, Trans. Am. Inst. Min. Eng. **7**, 91.

[2] "Ueber die Brechungsexponenten der Metalle," Ann. der Phys. Wied. **34**, 469.

[3] "On the Production of Transparent Films by the Electrical Discharge in Exhausted Tubes," Am. J. Sci. (3) **13**, 49; **14**, 169.

[4] "On Films produced by Vaporised Metals and their Applications to Chemical Analysis," Proc. Roy. Soc. **46**, 88.

[5] "On Electrical Evaporation," Chem. News **63**, 287.

those of low atomic weights showing, as a rule, more resistance than the heavier metals to the action of the spark. According to Crookes, this power of resistance does not increase regularly as the atomic weight decreases. No relationship has yet been discovered between the degree of electrical volatility and any known constant. Some relationship might be discovered if the volatilisation were carried on under such conditions of temperature and pressure as would most likely insure similar molecular conditions in each case. This might possibly involve the melting-point, as well as the atomic weight, as a factor.

If the order of the electrical volatility of the metals as found by Crookes be compared with Lothar Meyer's curve of atomic volumes, it will be found that the volatile metals lie at or near the minima of the curves, close together on the ascending sides in the periods IV, V and VII, alternating from one to the other. Magnesium and aluminium, which are practically non-volatile, lie on the descending side of period III. Aluminium, which is less difficult to volatilise than magnesium, is nearer the minimum of the curve. The metals given in the order of their electrical volatility alternate in the periods as follows:

Metal.	Comparative Electrical Volatility.—Crookes.	Period.
Pd	108.	V
Au	100.	VII
Ag	82.68	V
Pb	75.04	VII
Sn	56.96	V
Pt	44.00	VII
Cu	40.24	IV
Cd	31.99	V
Ni	10.99	IV
Ir	10.49	VII
Fe	5.50	IV

A thin, reguline and coherent film of a metal transmits light of a color remarkably similar to that emitted by its incandescent vapor. The color of the vapor of a metal varies with the temperature. Just above its boiling-point the vapor of sodium is purple; at incandescence, yellow. The vapor of potassium is green; at incandescence, violet. Silver in distilling gives off a blue-white vapor, while that volatilised by the electric arc passing between silver electrodes emits yellowish-green light. The color of the film obtained in many cases agrees very well with that of the incandescent vapor. In some instances, however, there is no similarity (see table below), a fact which is probably due to failure to obtain the proper conditions for the volatilisation and deposition. The perfection and continuity of the deposit is easily destroyed by very slight changes in the conditions. For instance, the aluminium film deposited by Wright by condensed sparks was brownish, while that observed by Fleming,[1] which resulted from the volatilisation of an aluminium connection in an overheated incandescent lamp, was of a "fine blue" color in the thinnest portions.

The color of the incandescent vapor of a metal is the resultant of the colors of the various rays emitted, and depends on the number and intensities of these rays; the color can therefore be fairly predicted on examining a table of the wave-lengths and relative intensities of the spectral lines of the metal.

I give below a table containing a number of metals, in which is given the color of the films by transmitted light, and the color of the incandescent vapor as observed and as indicated from the spectral lines. The authorities are given as far as possible. In some cases I have been unable to find any mention of the color of the incandescent vapor, although I am sure it must have been observed. In such cases I put my own name.

The color of a film will vary somewhat with the thickness, but as far as I have observed the colors extend over a very limited portion of the spectrum. Each metal possesses a strong tendency toward a characteristic color which is produced when the film is as thick as it can be to transmit any light.

ABSORPTION SPECTRA OF METALLIC FILMS.

Many of the films which corresponded closely in color to the incandescent vapor of the respective metals were examined carefully as to their absorption spectra by throwing a powerful beam of white light through them. If the same molecular condition existed in the film as in the incandescent vapor we would expect to have the same absorption. In other words, the dark lines of the absorption spectrum of the film should coincide with the bright lines of the emission spectrum of the incandescent vapor. I found in every case, however, that the films gave simply general absorption, no bands or lines being indicated.

SCHOOL OF CHEMISTRY, VANDERBILT UNIVERSITY, *February*, 1892.

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[1] Discourse delivered at the Royal Institution, The Electrician **24**, 393.

METAL.	COLOR OF FILM.	OBSERVER.	COLOR OF INCAND. VAPOR.	OBSERVER.	Color of Incand. Vapor as indicated by spectrum.
Gold Heated to 316° " on glass	Pinkish, violet, blue, blue-green Green Red Red	Faraday, Wright and others Crookes and others Faraday and Wright	Green	Dudley	Green
Silver	Deep blue	Wright	Blue Yellow-green in electric arc	Stas Dudley	Yellow-green
Copper	Green	Wright, Fleming	Green	Dudley	Green
Aluminium	Fine blue Brownish	Fleming Wright	Green-blue	Dudley	Green-blue
Bismuth	Gray-blue	Wright	Blue, slightly greenish	Dudley	Blue-green
Platinum	Blue-gray Purple	Wright Dudley	Blue (?)	Dudley	Blue
Palladium	Smoky brown	Wright	Green	Deville and Debray (?)	Green
Lead	Smoky brown inclining toward olive	Wright	Blue	Dudley	Blue
Zinc	Gray-blue, less deep than Ag, deeper than Bi.	Wright	Green-blue	Dudley	Green-blue
Cadmium	Gray-blue, about same as Zn, slightly less intense	Wright	Green	Dudley	Green
Magnesium	Gray blue, similar to Zn and Cd, but less clear	Wright	Green	Wright	Green
Tin	Brown-gray	Wright	Blue (?)	Dudley	Blue-green (?)
Iron	Neutral tint with faint tinge of brown	Wright	Green-blue	Dudley	Green-blue
Nickel	Gray or brown-gray	Wright	Blue-green	Dudley	Blue-green
Cobalt	Gray or brown-gray	Wright	Green-blue	Dudley	Green-blue
Tellurium	Dull purple	Wright	Golden yellow	Gernez	Orange-yellow
Potassium	Blue-violet	Dudley	Violet	Davy	Violet
Sodium heated on glass.	Brown-yellow	Dudley	Yellow	Davy	Yellow
Lithium heated on glass	Dark brown-red	Dudley	Red	Arfvedson (?)	Red

THE VOLUME LAG AND ITS BEARING ON MOLECULAR CONSTITUTION.

BY C. BARUS.

1.[1] In studying the relation between melting-point and pressure I came across a series of phenomena, the nature of which it was necessary to elucidate before the general problem could be attacked. I found the pressure necessary to solidify a substance decidedly greater than the pressure at which it again passes into the liquid state, *caet. par.* At first sight it seemed reasonable to suppose the differences so obtained could be referred to heating effects on compression and to cooling on expansion; but the magnitude of the pressure interval observed is often too large for this interpretation (palmitic acid). Solidification and fusion are almost instantaneous, provided pressure vary by a step exceeding the lag limit. Moreover, the simple statement given does not bear inspection. If the substance be liquid at pressure p and temperature t, then immediately after solidification by pressure the conditions are $p + \delta p$ and $t + \delta t$. If now $p + \delta p$ be reduced to p, and the substance remain solid, its temperature must be t', where $t + \delta t > t' > t$. The converse holds on liquefying. Hence, virtually, the substance is liquid at a lower temperature and higher pressure, and solid at a higher temperature and lower pressure than the mean values, and hence the occurrence of lag is really accentuated by the thermal discrepancy.

Relative to the character of these phenomena, pressures admit of a much more finely graded variation than temperatures. By applying pressures isothermally it may therefore be possible to demonstrate the generality of occurrences which have a counterpart in the retarded solidification of a substance either from fusion or from solution. Aside from these inferences, the interpretation to be given can be decided by a time criterion. If the maximum pressure at which the substance just remains liquid persistently exceeds the minimum pressure under which it just remains solid, *caeteris paribus*, then the observed phenomenon is a true volume lag.

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[1] The paragraphs are not numbered consecutively, but in agreement with a larger article. Let me say here that throughout the paper the terms volume lag and hysteresis are used in ways essentially alike.

I may conveniently insert a few special examples from my notes here. Caprinic acid is easily cooled below its melting-point (30°). To solidify it in this condition (say at 29°) requires at least 400 atm. To remelt it at the same temperature would only be possible under negative pressure, *i. e.* under a definite deduction from the internal pressure of the substance. Similarly, but more remarkably, thymol, though melting, say at 50°, can easily be undercooled to 28° and less. At 28°, at least 500 atm. are necessary to solidify it. In spite of the larger interval of undercooling, larger pressure is essential for solidification than in the preceding case. Again, para-toluidine, melting at 45°, is only solidified at 28° (undercooled) by pressures of about 500 atm. Obviously, these phenomena are independent of heating by compression.

3. My experiments[1] on melting-point and pressure differed from those of my predecessors, inasmuch as I made the volume changes due to pressure acting at constant temperature, a criterion of the state or condition of fusion. The substances were enclosed in glass capillary tubes, kept at the desired temperature by a vapor-bath (boiling tube of the kind described in detail elsewhere).[2] It was frequently necessary to boil under diminished pressure in order to obtain convenient temperatures of solidification. The upper end of the capillary being suitably closed, the lower was put in connection with a large Cailletet force-pump.[3] A measured pressure was thus applied at pleasure by pushing the thread of mercury in the lower end of the capillary against the substance. The way in which the mercury thread advances is characteristic. So long as the substance is liquid, the thread rises directly in contact with the substance, and capped by an unbroken meniscus. When solidification commences the meniscus is soon broken and pointed, and the thread eventually runs up between walls of the solid compressed substance. When pressure is withdrawn again, it frequently happens that small threads of the mercury column have actually broken off. The reason for this behavior is at hand: on solidifying, the column contracts markedly from the axis of the tube radially outward, leaving the core in a vacuous, spongy state. Into this central sponge the additional pressure forces the finer filament of mercury by breaking the dissepiments. Usually a good criterion for the occurrence of solidification is given by the

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[1] The apparatus is shown in Am. J. Sci. **39**, 6 (1890).

[2] Bull. U. S. G. S. **54**, 88 (1889).

[3] Made both by Ducretet and the Société Genevoise. Capacity, 1000 atm.

optical change from clear to opaque. Thus, in case of paraffin, a white thread shoots, as it were, through the axis of the originally clear capillary.

4. The present paper was written some two years ago,[1] and I then provided a full series of results of the volume lag observed in palmitic acid, naphthalene, monochloracetic acid, and paraffin. With my present facilities and experience, however, I am able to improve on this work considerably. I have therefore here withdrawn the original data, merely stating that I have them in hand and that they were obtained by the capillary-tube method just described. Data sufficient for my present purposes are given in my more recent work on the continuity of solid and liquid.[2] To fully exhibit the hysteresis, volume should be mapped out as a function of time, using pressure as a parameter. The curves so obtained are persistently asymmetrical when the isothermal march is made alternately from liquid to solid and from solid to liquid.

Discussion.

8. The first point of view from which these data are to be studied is that of the thermodynamic cycle and relative to $\int pdv$. It also involves a consideration of James Thomson's doubly-inflected isothermals. The discussion, however, is best omitted here, and will be made elsewhere.

9. Before proceeding further, it is expedient to insert a definite view as to the underlying causes of the liquefaction of a gas and of the solidification of a gas, or a liquid. I shall employ the current chemical terminology, and explain my meaning more fully in the course of the paper, §§22, 25. My hypothesis is that change of the state of aggregation is brought about by, and is evidence of a corresponding change of the (cohesive) valency in one or more of the constituent atoms of the substance. Valencies are added in successively decreasing intensity. More sharply:

(1) A liquid or gas solidifies whenever, in consequence of changes of the physical or chemical environment (temperature, stress external or internal, etc.), the valency of the constituent atoms is sufficiently increased to admit of the permanent construction of a continuous tridimensional chain, the type structure and the molecular weight of which (solid) are each a multiple of the given structure and molecular weight.

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[1] Cf. Am. Journal **38**, 408 (1889).

[2] Am. Journal **42**, 140 *et seq.* (1891).

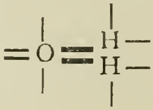
(2) A gas liquefies whenever, in consequence of changes of environment, the valency of one or more of the constituent atoms is sufficiently increased without affording means for the permanent construction of the tridimensional chain in question.

Suppose the molecule of a gas be called free. Then the molecule which is free to move along a wall of similar molecules (and such may be the case at the surface of some liquids and solids) may be said to have lost one degree of freedom; if it is constrained to move in the angle between two such walls, it has lost two degrees of freedom. Finally, with the same understanding in mind, the solid molecule has lost three degrees of freedom. Thus, as will appear more clearly below, the three states of aggregation are related to the three dimensions of space.

The criterion by which (1) and (2) are obtained is compressibility; for I have merely supposed that when compressibility suddenly and phenomenally increases (as it does at liquefaction and solidifying points), the inherent cause is an increase of valency, whereby external pressure is now reënforced by internal pressure.

It does not follow from (1) and (2) that a fluid may not exist below the corresponding liquefying or solidifying points. Elsewhere[1] I inferred that, as regards isopiestic thermal expansion, the liquid and the solid, as well as the gas, obey certain ideal laws, which may be conceived to hold good on both sides of the points in question, quite apart from the usually gratuitous hypothesis of polymerism. Seeing that a given state of aggregation maintains its labile equilibrium through a wide range of changes of condition (cf. §1), one calls to mind certain results of the hydraulic experiments of Osborne Reynolds. Cf. §25.

10. Some illustration of the preceding paragraph is desirable. For instance, it is impossible to construct the tridimensional chain out of $O''H'$. Nor is this possible[2] with $O^{IV}H'$ or $O''H'''$. With $O^{IV}H'''$, the solid chain, if possible, would necessarily be an exceedingly complex structure. With $O^{VI}H'''$, a symmetrical in two dimensions, possessing hexagonal symmetry, may be made from the type structure



$$=\overset{|}{\underset{|}{O}}=\begin{matrix}\overset{|}{H}-\\ \underset{|}{H}-\end{matrix}$$

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[1] Proceedings Am. Acad. **26**, 315 (1891).

[2] The possibility of trivalent, pentivalent, etc., hydrogen is discussed by Geuther (Jenaische Ztschr. (2) **6**, 119). Cf. Lothar Meyer, **9**, 333 (Breslau, 1884).

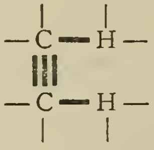
and for $\mathrm{O}^{\mathrm{x}}\mathrm{H}^{\mathrm{vii}}$, the same structure is possible in three dimensions. In the diagram, principal affinities are indicated by heavy lines, added affinities by light lines. They may be verbally distinguished as molecular and cohesive affinities, respectively.

Before reaching this extreme stage, a number of possible types have been passed, any one of which may possibly characterise the liquid molecule.

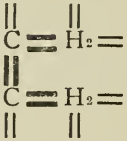
The conception thus gained of the gaseous and the solid states is clear-cut. The conception of the liquid states is apparently vague. It is at most a transitional stage. This, however, appears to me to be an advantage. It is in keeping with what is usually implied in the term liquid. The liquid molecule is constantly undergoing changes as regards the number of individuals which make up a single nomadic colony, without breaking up the type molecules out of which the colony is put together. The external effect of the exchange of the superfluous valencies, as it were, is exhibited in the cohesion of liquids. It determines the conditions of miscibility and of solution. It is further active in capillarity; §19.

Note that, compatibly with the hypothesis given, a liquid is by no means necessarily a conductor of electricity. Cf. §9.

11. Evidence in favor of the view here advocated is given by the existence of any homologous chemical series, each member of which may in general occur in the three states of aggregation. If $A_l\, B_m\, C_n \ldots$ be any compound, and if the valency of each atom be cohesively increased $2x$ (following the order 1, 3, 5, 7 .... or 2, 4, 6, 8 ...), then there will be $2x\,(l + m + n)$ new bonds to combine with the $2x\,(l + m + n)$ new bonds of each of the contiguous molecules, to form a suitable tridimensional chain, without breaking the integrity of the original molecule of the gaseous state. More generally, $2x$ may be regarded different for each atom. Thus, for instance, solid acetylene may be typified by



where molecular affinities are denoted by heavy lines, and each light line (cohesive affinity) may be x or x'...fold, for carbon and hydrogen, respectively. Similarly, solid ethylene is typified by



$$\begin{array}{ll} \| & \| \\ C = & H_2 = \\ \| & \\ C = & H_2 = \\ \| & \| \end{array}$$

In the same way the character of solid isomers or of allotropic differences is retained. Supposing all the atoms accounted for, the negation of an increase of cohesive valency would necessitate a passage of $3C_2H_4$ into $2C_3H_6$ or into some higher homologue. This, however, is quite beyond the power of mere liquefaction or of solidification, generally speaking.

13. The views stated in §9 apply equally well whether solidification takes place after fusion or after solution. They suggest the function of water of crystallisation in many cases of solidification. In such instances, the (cohesive) valencies of the atomic constituents both of the water and of the dissolved salt have increased under the conditions stated in §9, (1), in such a way as to admit of the construction of the solid framework.

14. Instances of the availability of the present views in accounting for the properties of colloidal solutions, and for analogous phenomena in sedimentation, have been given elsewhere.[1] The ejection of dissolved gases by most liquids on solidifying is an allied example.

16. It follows, from §9, that molecules near the surface will be least favorably situated for stability; §18. In quiescent friction the conditions of occurrence seem to be such that time is given the molecules at the surface of contact of two bodies to interlock; §9.

17. It is the immediate result of §9 that when the valencies are reduced by heat to those which appertain to the gaseous state, the construction of a solid chain or of a liquid chain is impossible under any pressure. This begins to occur at Andrews' critical temperature. Again, when the valencies are reduced by heat to those which appertain to the liquid state, the construction of a tridimensional chain is equally impossible under any pressure. This suggests a lower critical temperature,[2] or, in other words, an eventual continuous passage from the solid to the liquid state by pressure.

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[1] Barus and Schneider, Ztschr. phys. Chem. **8**, 289 (1891); Am. Journal **42**, 366-67 (1891).

[2] Cf. §4.

18. It was stated, §18, that surface molecules are probably least stable, since it is here that the cohesive affinities must unite among themselves in a way different from the body of the chain. This suggests the occurrence of volatilisation, evaporation, and greater tendency to break up in those parts. Viscosity, on the other hand, is the physical expression of internal imperfections of the solid chain.

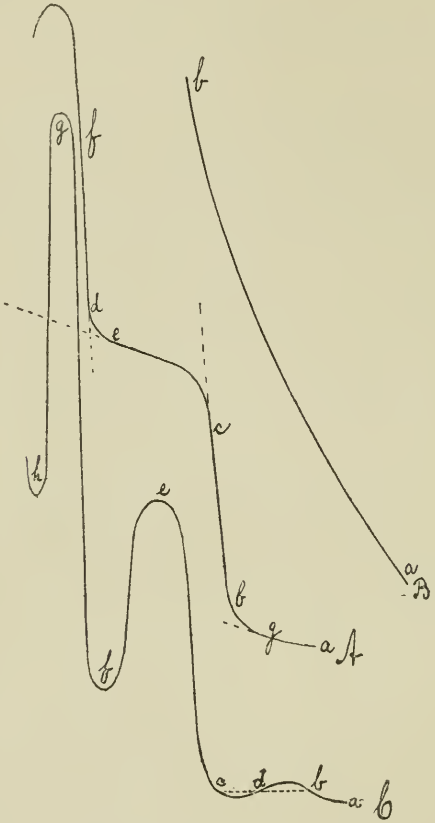
19. Again, the state of the surface may be considered in relation to capillarity; §10. The free affinities at contiguous surfaces are available for combination. At Andrews' critical temperature, the absence of marked capillary phenomena[1] demonstrates the absence of a possible solid or liquid chain. This is in accordance with §17. According to Hannay and Hogarth,[2] solution by no means ceases at the critical temperature. It is to be remarked, however, that neither is the gaseous molecule here exclusively present, since the lag (§§20, 21) has not wholly disappeared, nor is the critical temperature of a solution identical with that of the solvent.

20. The next step in the present considerations is the interpretation of lag phenomena as intimated in §8. My endeavor is to find a suitable lag mechanism. The variation of molecular force p_x with the mean distance apart x of the molecules acted on, may be represented by the horizontal push necessary to move a heavy point frictionlessly along a curve in a vertical plane. If α_x be the angle which the tangent at any point P of such a curve makes with the horizontal, then $p_x = g/\tan \alpha_x$ is the horizontal force necessary to hold the point of weight g in equilibrium at P. Hence $\alpha_x = \tan^{-1} g/p_x$ is the inclination to be given the curve at every point P whose abscissa is x, in order that motion along the curve in question may reproduce any stated variations of p_x. Finally, the position of P with reference to the vertical, *i. e.* its height above some fixed horizontal datum line, expresses the molecular potential energy under the given conditions of compression; §24. Similarly, the kinetic energy of the point may be utilised; for it is clear that when α_x lies between $\pi/2$ and π, p_x will be negative; and if negative pressure is excluded from consideration, it follows, from the principle of conservation, that whenever increasing α_x passes through $\pi/2$, molecular energy will change

[1] Mendeleeff, Pogg. Ann. **141**, 618 (1870).

[2] Hannay and Hogarth, Nature **120**, 82 (1879); Proc. Roy. Soc. Lond. **30**, 178 (1880); Chem. News **41**, 103 (1880).

from potential to kinetic. In how far negative values of α_x, corresponding to reëntrant figures, cannot be disregarded, will presently be stated.



In virtue of the occurrence of lag, the curve of motion will be harmonic. The annexed figure represents the series of phenomena here in question, apart from dimensions which cannot be clearly reproduced in the drawing. The mean distances between contiguous molecules are denoted by abscissæ. The curve *A* is first to be considered. Suppose it to start from *a*, the pressures or horizontal forces necessary to move it along the curve constantly increase until the point *c* is reached. From here on pressure, if kept constant, is in excess, and hence the point moves onward as far as *d*. To move it further, pressure must again increase. Suppose now that after arriving at *d*, pressure is decreased. The point will at first move but slightly until in its retrograde march *e* is reached. After this, if pressure decreases further, the point will at once fall to some position *g*. For the purpose of the present diagram this kinetic energy of the point is disregarded.

Here, therefore, is the mechanism for a lag. Along the branch *agc* the substance is fluid, along *df* it is solid, and *ced* represents the transitional state from liquid to solid. The phenomenon is a temporary lag. Its occurrence is evoked by pressure, and after pressure has reached the original value at *a*, the effect of the lag is nil, since the point is also at *a*.

Manifestly the character of the curve *A* depends on temperature. Suppose temperature to be raised sufficiently above the corresponding critical point of the substance; then the lag will have wholly disappeared, and compression will take place along some curve *B* without harmonic contour.

21. Again, let temperature be decreased. Then the temporary lag *ced* of the curve *A* will become more pronounced in its harmonic curvature, and take some form *C*. To bring out the character of this diagram it would be necessary to apply pressure negatively, a problem experimentally impossible unless the whole phenomenon be exhibited by heat. For the sake of fixing ideas, however, suppose the substance at the low temperature in question to be imponderable. Suppose, too, that by some ideal means the individual molecules are all kept at the required distance apart, so that there is no nuclear condensation. Then, as pressure is applied, the point representing the changes of state when molecules approach each other will move along a curve *C*. There will be lag at *bdc* coincident with the passage from gas to liquid, and lag at *ef* coincident with the passage from liquid to solid. The lags so encountered, *i. e.* by these ideal means, will, however, be permanent, and therefore be an advanced state of the lag given in *A*; for the point remains in the valley after pressure is withdrawn.

In substances which, like thymol, can be undercooled, it is actually possible to produce a permanent lag corresponding to *cef* of the curve *C*, as was pointed out in §1. Explosion of a gas mixture like OH_2 by pressure alone is an allied instance.

Negative values of α_x corresponding to negative pressures are introduced by such substances as expand on solidification. The considerations here presented are peculiar; for, in a march of the kind just described, *i. e.* with continual volume reduction, the liquid-solid lag would not at all appear.

22. The question now arises whether the two lags specified are the only ones which would occur in a general march of the kind here specified; in other words, has the curve any characteristic prolongation to the right and to the left? The first question is easily answered. Let successive constant temperatures at which condensations take place be selected, so that the body is kept in the field of the successive changes. In a passage toward the right the conditions of dissociation are encountered; and there must be a corresponding lag, permanent under suitable temperature conditions, in that region. Does the curve C terminate on the left at g? I believe that if solid matter is sufficiently compressed there must ultimately occur another lag of high-pressure order. Under proper conditions of temperature this extreme lag will be permanent, and will represent the passage of the given atom into the next consecutive of a series of atoms of increasing atomic weights. This is shown at gh in the figure. Again, toward the extreme right and beyond the field of dissociation, if the process of analysis be pushed further, another region of permanent lag will be passed through, representing the transfer of the given atom into the next consecutive of a series of atoms of decreasing atomic weights.

It will be noticed that the occurrence of lag is coexistent with the occurrence of cohesive affinities, as stated succinctly in §9.

23. Having thus supposed that affinities may be grouped in different orders, that primitive affinities are active in the atom, and that the coherence of the atom occurs in virtue of a volume lag of high-pressure order, these views account for vast aggregations of atoms of like kind. They are the products of a given order of lag.[1] The views also suggest a uniform scheme for the successive evolution of atoms, and are therefore in harmony with the periodic classification of elements. In general, a law of distribution is implied, by which the occurrence of any given dimension of ultimate particle is specified.

24. If it be supposed that each atom is wholly or partially surrounded by a molecular field of attraction, of definitely circumscribed dimensions and of equally definite contour, the occurrence of hysteresis necessarily accompanies any marked change of volume. There may be a series of such fields of force, either distinct, or symmetrically within each other. From this interpre-

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[1] The laboratory being the interior of a sun or planet, for instance.

tation the diagram *C* at once follows. It was stated, §20, that the vertical height of the point in moving frictionlessly along the curve, above some fixed datum, is the expression of its potential energy. Hence, if the bounding surface of any field be a region of maximum potential relatively to the space on either side of it, the lag is permanent. If the bounding surface be a region at which the space-rate of change of potential is pronounced but does not pass through zero, the lag is temporary. It follows that chemical combination, change of state from gas to liquid, from liquid to solid, are successive stages of a periodically recurring volume lag. It follows also that the pronounced harmonic character of the space variation of molecular force at low temperatures gradually flattens out, and finally quite loses the said harmonic character at very high temperatures. Finally, the cohesive affinities of §9 may each correspond to special and distinct fields of atomic force; or they may result from the invasion by an atom, of the unoccupied space of a relatively large field of molecular affinity.

24*a*. I have attempted to associate these fields of force with an ether environment kept in a dynamically structural state by vibrating corpuscles (atoms or molecules); I have also given some consideration to the known behavior[1] of the vortex atom; but all this is far beyond the scope of the present paper, in which it is merely my object to see whether something may not be gained by supposing cohesive forces and affinities to be essentially the same in kind but differing in their respective orders of intensity.

25. It is in place, finally, to enumerate some other lags, and to refer them to the type lag of §§20, 21. Among these, phenomena of retardation at melting- and boiling-points, retarded fusion, undercooling, retarded condensation, superheating, are prominent. They have been virtually included in the preceding paragraphs, and therefore need not be touched upon again. The same is true of supersaturation in case of solution.

Lag phenomena are clearly observable in case of metals subjected to stress. By applying tractions, alternately increasing and decreasing between wide limits, Ewing[2] demonstrated the occurrence of lag thermo-electrically. In an earlier paper of Cohn[3] a similar method is pursued with the same results. Quite recently

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[1] J. J. Thomson: A treatise on the motion of vortex rings. Macmillan, 1883, pp. 71 to 124.

[2] Ewing, Phil. Trans., London, 2, 361 (1886).

[3] Cohn, Wied. Ann. 6, 385 (1879).

O. Schumann,[1] availing himself of Braun's[2] deformation phenomena, investigated a new lag by measuring the electrical resistances of a stretched helix of nickel wire.

The same class of phenomena are exhibited with singular clearness in case of magnetisation. They were first definitely pointed out and studied by Warburg,[3] though the questions had been elucidated by Fromme[4] and by Auerbach.[5] Ewing[6] made them the subject of an elaborate and independent research. Iron is operated on by magnetic fields alternately increasing and decreasing between stated limits, and the resulting induction compared with the intensity of the field at each stage of progress.

In studying the magnetic behavior of stretched and twisted nickel wire, Nagaoka[7] (and, I believe, Wiedemann, though I cannot now find the experiments after much searching) obtained definite cyclic variations due to torsion.

In all these cases the effect of stress is a lag of the nature of that described in curve *A*. Molecules, in favorable positional relations, are urged either into or out of the molecular fields of force of contiguous molecules, and the change of structure resulting is indicated mechanically, electrically or magnetically.

To these instances the remarkable discovery made by Osborne Reynolds[8] in studying the flow of liquids in pipes is to be added, since it is through this that a deeper insight into hysteresis may possibly be gained. According to Reynolds, " . . . if there were a critical velocity at which, for any disturbance whatever, the water became stable, this velocity was much less than that at which it would become unstable for infinitely small disturbances; or, in other words, suggesting that there were two critical values for the velocity in the tube, the one at which steady motion changed into eddies, the other at which the eddies changed into steady motion."

26. I have carried these considerations into much greater detail by applying them to electrical and magnetic phenomena, but the above paragraphs suffice to exhibit the point of view taken. It has been my endeavor to frame a working hypothesis which shall not be at variance with known facts of physics or chemistry, and which shall be sufficiently flexible to imply clear-cut conditions for the series of volume phenomena which I am investigating.

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[1] Schumann, Wied. Ann. **38**, 256 (1889).

[2] Braun, Wied. Ann. **37**, 97, 107 (1889).

[3] Warburg, Wied. Ann. **13**, 141 (1881).

[4] Fromme, Ibid. **4**, 76 (1878); Ibid. **13**, 318 (1881).

[5] Auerbach, Ibid. **14**, 308 (1881).

[6] Ewing, Phil. Trans. of London, **2**, 523 to 640 (1885).

[7] Nagaoka, Phil. Mag. (5), **27**, 117 (1889).

[8] Reynolds, Phil. Trans., London, **3**, 935 (1883); cf. p. 957.

ON CITRONELLONE, AN UNSATURATED FATTY ALDEHYDE.

By Edward Kremers.

In a paper read before the American Pharmaceutical Association in 1887 I presented a preliminary chemical examination of the citronella oil of commerce, with a review of the botanical and chemical literature of the different andropogon oils. In connection with this review, the fact was repeatedly pointed out that more or less confusion existed regarding the origin and composition of these oils. From my remarks on the "Production of the Oil" it could easily be inferred where the causes for such discrepancies were to be sought. So long as the manufacture of these products remains in the hands of ignorant natives, commercial articles sold under the same name may or may not be identical. It is therefore useless, under these conditions, to criticise the results of one investigator when they differ from those of another. The prime object of examining the andropogon oils at present must be to separate and study carefully the chemical characteristics of the substances they contain. It is only after knowledge has been thus attained that we shall be able to ascertain the exact composition of the various oils in question, having been distilled by reliable men, and from grasses identified by experts. This being accomplished, we can demand that the commercial oils be thereafter of uniform composition.

Since 1887 two chemists have taken up the subject of the andropogon oils: Mr. Frank D. Dodge, whose results have been published in this journal,[1] and Dr. F. W. Semmler.[2] I do not wish to compare the results obtained by Mr. Dodge with mine, for the above mentioned reason. Others have carried the comparison of our results to a point well-nigh ridiculous. But I object if Mr. Dodge and others compare the aldehyde bodies obtained by us, for my aldehyde by analysis was shown to possesss the formula $C_7H_{14}O$, whereas Mr. Dodge assigned to his aldehyde the formula $C_{10}H_{18}O$. As to the "citronellon" of Dr. Semmler, I would state that German melissa oil is a very questionable article. Dr. Bertram, in a private communication, has kindly informed me that the firm of Schimmel & Co. have never been able to obtain more than traces of an oil from German balm. The term "citronellon" has been applied rather indiscriminately to aldehyde-like bodies from various oils. The "citronellon" examined by Dr. Semmler was isolated by him from citronella oil, whereas the bulk of commercial citronellon is obtained from the oil of *Eucalyptus maculata*, var. *citriodora*.[1]

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[1] This Journal **11**, 456; **12**, 553.

[2] Ber. d. chem. Ges. **24**, 208.

Though there may be but little doubt regarding the identity of "citronellon" from various sources, yet it would be better to ascertain the facts before making any general statements. The literature of volatile oils is sufficiently complex indeed, and it should be our endeavor to simplify it rather than to add to its complexity.

The substance which has furnished the subject for this preliminary paper is the so-called *citronellon* from the oil of *Eucalyptus maculata*, var. *citriodora*. It was isolated from the oil by the chemists of Messrs. Schimmel & Co., Leipzig, and was generously given me for investigation.

The citronellone from this source is a colorless oily liquid of a lemon-like odor not at all disagreeable. Its specific gravity is 0.875 at 17.5°, and 0.871[2] at 20°. It rotates the ray of polarised light to the right 7.127° in a 1-dm. tube. Hence $[\alpha]_D = +8.18°$. The citronellone used in excess in the oxidation experiments with alkaline permanganate solution, after distillation with water vapor and drying over calcium chloride, possessed a specific gravity of 0.866 at 20.5°. In this case $[\alpha]_D = +8.220°$. Fraction 92°–95°, obtained by distilling citronellone under a pressure of only 15 mm., had the specific gravity 0.8632 at 20°. In a 2-dm. tube it rotated the ray of polarised light 15.858° to the right. Hence $[\alpha]_D = +9.18°$.

An attempt to distil the crude citronellone under ordinary pressure resulted in an entire failure. The following fractions were collected:

A = 98°–105° — a small quantity.
B = 195°–210° — less than one-third.
C = 215°–220° " " "
D = 280°–310° " " "

Fraction A developed upon standing an agreeable minty odor. Fraction B possessed a mixed odor; specific gravity 0.875 at 21°; $[\alpha]_D = +6.81°$. Triturated in a mortar with a molecular quantity of sodium acid sulphite and a few drops of water, a solid dry mass resulted which soon became almost odorless. Fraction

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[1] Schimmel & Co., "Bericht," Oct. 1890, p. 21.

[2] 0.873 at 15°.

C resembled B. Fraction D was a yellowish liquid of decided fatty odor; specific gravity about 0.902 at 22.5°; rotatory power in a 1-dm. tube about —3 455°. Treated with sodium acid sulphite like fraction B, it combined but partially with the salt. *It is noteworthy to observe the change in the action upon polarised light.*

Under a pressure reduced to 15 mm. but very little came over below 92°; about one-half came over between 92°–95°, and about one-third between 95°–97°. The mercury then rose quickly to 110°, when there remained in the flask a viscid yellow liquid.

The citronellone recovered from the oxidation experiments with permanganate, after being dried over calcium chloride, yielded the following results upon analysis:

I. 0.1475 gram gave 0.1718 gram $H_2O = 0.01908$ gram H, and 0.4178 gram $CO_2 = 0.11394$ gram C.

II. 0.1618 gram gave 0.1825 gram $H_2O = 0.02027$ gram H, and 0.4565 gram $CO_2 = 0.12450$ gram C.

III. 0.1064 gram gave 0.1240 gram $H_2O = 0.01377$ gram H, and 0.3007 gram $CO_2 = 0.082009$ gram C.

The following results were obtained from fraction 92°–95° distilled under a pressure of 15 mm.:

IV. 0.3102 gram substance gave 0.3310 gram $H_2O = 0.03677$ gram H, and 0.8781 gram $CO_2 = 0.23948$ gram C.

V. 0.2300 gram substance gave 0.2458 gram $H_2O = 0.02731$ gram H, and 0.6475 gram $CO_2 = 0.17659$ gram C.

VI. 0.3064 gram substance gave 0.3180 gram $H_2O = 0.03533$ gram H, and 0.8583 gram $CO_2 = 0.23408$ gram C.

VII. 0.2573 gram substance gave 0.2727 gram $H_2O = 0.03030$ gram H, and 0.7230 gram $CO_2 = 0.19718$ gram C.

	Calculated for		Found.						
	$C_{10}H_{18}O$.	$C_{10}H_{20}O$.	I.	II.	III.	IV.	V.	VI.	VII.
C	77.92	76.92	77.24	76.94	77.07	77.20	76.77	76.39	76.63
H	11.69	12.82	12.93	12.52	12.94	11.85	11.87	11.53	11.77

These results on the whole do not agree better for $C_{10}H_{18}O$ than for $C_{10}H_{20}O$. However, the chemical behavior of the substance demands the adoption of the former formula. Analyses V. and VII. I have reason to consider the best, and the results calculated from these correspond fairly well with the formula $C_{10}H_{18}O$.

Citronellone and Bromine.

Citronellone readily decolorises bromine; 10 cc. citronellone, dissolved in 30 cc. glacial acetic acid and kept cold by ice, decolorised not quite 3 cc. bromine. The equation

$$\underbrace{C_{10}H_{18}O}_{154} + \underbrace{Br_2}_{160} = C_{10}H_{18}Br_2O$$

requires 2.8 cc. bromine. This proves more conclusively than the determination of the molecular refraction of a substance not chemically pure, that there is a double bond in the molecule, and that the formula therefore must be $C_{10}H_{18}O$, and not $C_{10}H_{20}O$.

The bromine addition-product is unstable and could not be obtained in a crystalline condition. Upon standing, the liquid blackened and hydrobromic acid was given off. Heated with an alcoholic solution of potassa, bromide of potassium was abundantly precipitated. The product was distilled with water vapor. The aqueous distillate possessed an agreeable minty odor. By extraction with ether, a few cubic centimetres of an oil were obtained which had a decided peppermint odor. Most of the oil had been resinified, and was not volatile with water vapor. A repetition of the experiment upon a somewhat larger scale yielded about 10 cc. of oily distillate, which upon redistillation was resolved chiefly into two fractions, boiling from 200°–210° and from 210°–220° respectively. These fractions have a decided peppermint odor, a characteristic property which has been produced in various reactions. This substance promises to be of some interest and will be further examined.

Citronellone and Sodium Acid Sulphite.

The citronellone under consideration was separated from the other constituents of the eucalyptus oil by means of its crystallisable sodium acid sulphite compound.[1] From this it was regenerated with the aid of sodium carbonate. That the compound had not suffered any change was readily shown by the fact that it again combined with sodium acid sulphite. The observation made by the chemists of Schimmel & Co., that the union of the two compounds is accompanied by a considerable rise in temperature, can also be confirmed. If molecular quantities of citronellone and sodium acid sulphite are triturated in a mortar, the latter will dissolve in the former, and upon the addition of a few drops of water the emulsion-like liquid will congeal. This method of preparing the addition-product is not connected with the loss caused by the use of a solution of the sodium acid sulphite. An attempt to add two molecules of sodium acid sulphite failed.[1] When to the citronellone a hot concentrated solution of sodium acid sulphite (two molecules to one of citronellone) was gradually added, a crystalline magma resulted which dissolved in more of the solution. It was then heated for several minutes on a water-bath. Upon cooling, a mass of crystals separated, which were freed from mother-liquid and dried on porous plates. This product was recrystallised from hot water, and the resulting crystals were dried as before. These air-dried crystals lost but from 0.15 to 0 3 per cent. of their weight when kept in a desiccator for a week. The sulphur was estimated by fusing with potassa and nitre, dissolving the product in water and precipitating the sulphuric acid as barium salt. To purify the barium sulphate it was fused with sodium carbonate, the mass dissolved in water, and the sulphuric acid again precipitated with barium chloride.

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[1] Schimmel & Co., "Bericht," Oct. 1890, p. 21.

I. 0.4418 gram substance yielded 0.3807 gram $BaSO_4 = 0.0522$ gram S.

II. 0.5995 gram substance yielded 0.4675 gram $BaSO_4 = 0.0641$ gram S.

Calculated for		Found.	
$C_{10}H_{18}O.NaHSO_3$.	$C_{10}H_{18}O(NaHSO_3)_2$.	I	II.
12.40 per cent.	17.67	11.81 per cent.	10.69

Citronellone and Hydroxylamine.

A condensation-product of these two substances was obtained by allowing hydroxylamine hydrochlorate and sodium bicarbonate to react upon an alcoholic solution of citronellone until carbon dioxide was no longer liberated, and then heating the mixture on a water-bath. The filtrate from the sodium chloride was allowed to evaporate spontaneously, but no crystals resulted. The oily liquid which separated was distilled under ordinary pressure, but decomposed, hydroxylamine being given off. An attempt to distil it under greatly diminished pressure was more successful. Water came over at first, and then, under a pressure of 12 mm., two-thirds of the product distilled over between 128°–133°. During the distillation crystals formed in the condensing-tube, but afterwards rėdissolved. The distillate was set aside in a cold place, but even after weeks no crystals reappeared. It has not yet been analysed. The oxime—for such it apparently is—takes up bromine: from solutions in ether and in glacial acetic acid the addition-product separated as a viscid oil; from the solution in petroleum-ether acicular crystals separated, not in sufficient quantity, however, to be further investigated. Condensation with phenyl-hydrazine has thus far given even less satisfactory results.

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[1] Comp. Heussler, Ber. d. chem. Ges. **24**, 1805; also, Dodge, This Journal **12**, 553. Dodge obtained from the aldehyde isolated from lemon-grass oil a compound with sodium acid sulphite, to which he assigned "the tentative formula $C_{10}H_{16}O.2NaHSO_3.4Na_2SO_3.50H_2O$." From the "dry salt" he obtained by analysis 22.48 per cent. sulphur, whereas the formula requires 22.6 per cent. Now the much simpler formula $C_{10}H_{16}O(NaHSO_3)_3$ requires 20.68 per cent. sulphur. The "citriodoric aldehyde" from lemon-grass oil, no doubt, has two double bonds. Perhaps a reaction takes place with this aldehyde similar to that Dr. Heussler has observed in the case of cinnamic aldehyde, although an analogous compound could not be obtained thus far from citronellone.

Oxidation of Citronellone with Ammoniacal Silver Oxide.

Citronellone was oxidised in the same way with ammoniacal solution of silver oxide that Semmler oxidised the aldehyde $C_{10}H_{18}O$ from oil of balm ("Melissenö"), and the aldehyde $C_{10}H_{18}O$ from citronella oil.[1] These substances he chooses to call "citronellon," and to regard them as identical with the "citronellic aldehyde" of Dodge[2] and with the "citronellon" of Schimmel & Co.,[3] although he had not experimented with the "citronellon" from eucalyptus oil to which Schimmel & Co. first applied the term "citronellon," and for which it should be reserved until the identity of these various aldehydes, $C_{10}H_{18}O$, from different sources has been proved.

The silver salt was obtained from the solution of the sodium salt as a white, curdy precipitate, and is by no means characteristic in appearance. The dried salt was analysed with the following results:

I. 0.2128 gram substance yielded 0.3417 gram $CO_2 = 0.09319$ gram C, and 0.1297 gram $H_2O = 0.01441$ gram H.

II. 0.3720 gram substance yielded 0.1420 gram Ag.

	Calculated for $C_{10}H_{17}O_2Ag$.	Found.
C	43.32 per cent.	43.79 per cent.
H	6.14 "	6.77 "
Ag	38.99 "	38.17 "

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[1] Ber. d. chem. Ges. **24**, 208.

[2] This Journal **11**, 462.

[3] Loc. cit.

Oxidation of Citronellone with Permanganate.

After a number of experiments, the following proportions were found to give the best results: To a solution of 12 grams of potassium permanganate in about 500 cc. of water, 12 cc. (*i. e.* an excess) of citronellone were added. The mixture was heated on a water-bath in a flask connected with a reflux condenser. When repeatedly shaken, the reduction of the permanganate was complete in less than an hour. The excess of citronellone was distilled off with water vapor, the remaining liquid filtered, and the filtrate evaporated on a water-bath. From 315 grams citronellone, 122 grams, or 38.7 per cent., were recovered;[1] 193 grams were oxidised.

The aqueous filtrate, containing the potassium salts of the acids formed by the oxidation, upon evaporation yielded two crops of crystals, chiefly oxalate and carbonate. To the mother-liquid dilute sulphuric acid (1:5) was added in slight excess; potassium sulphate was precipitated, and the liquid separated into an oily and an aqueous layer. The oily acid (112 grams) was of viscid consistency and of a reddish color. Attempts to prepare the sodium, calcium and barium salts directly yielded results not very satisfactory. When distilled under ordinary pressure a part of the crude acid came over between 300°–305°, but it was largely decomposed. When distilled under diminished pressure (reduced by 22 in.) an aqueous acid distillate came over first, but even under these conditions the contents of the flask soon underwent decomposition. The aqueous fraction when redistilled boiled between 100°–105°, and this distillate gave reactions for formic acid with ferric chloride, silver nitrate and mercuric chloride.

Distillation with water vapor was then resorted to. The acid distillate, from which no oil separated, when neutralised with soda also gave reactions for formic acid. The residue in the flask was perfectly clear—all the acid having gone into solution—and was shaken with ether; upon evaporation of the ether, a viscid liquid of slightly reddish color remained. When distilled (the pressure being reduced by 22 in.), water came over first, then about two-thirds of the oil at 220°, when decomposition set in and the distillation was interrupted. The distillate was viscid, but colorless. Dried in a desiccator over calcium chloride, it yielded upon analysis the following results:

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[1] More dilute solutions of permanganate apparently attacked the citronellone molecule more radically, since a larger percentage could be recovered unchanged. When 12 grams of citronellone were oxidised with 10.5 grams permanganate in 500 cc. of water, 55.5 per cent. of the citronellone was recovered. The same results were obtained twice. When 12 grams citronellone were oxidised with a solution of 21 grams of permanganate in 500 cc. of water, in one experiment 40.5 per cent., in another only 30.3 per cent. of citronellone was recovered by distillation with steam.

I. 0.4943 gram substance gave 0.9945 gram $CO_2 = 0.27122$ gram C, and 0.3830 gram $H_2O = 0.04255$ gram H.

II. 0.3682 gram substance gave 0.7514 gram $CO_2 = 0.20492$ gram C, and 0.2918 gram $H_2O = 0.03242$ gram H.

III. 0.2860 gram substance gave 0.5873 gram $CO_2 = 0.16017$ gram C, and 0.2267 gram $H_2O = 0.02518$ gram H.

	Calculated for		ound.		
	$C_{10}H_{18}O_5$.	$C_{10}H_{20}O_4$.	I.	II.	III.
C	55.04	55.82	54.86	55.65	56.00
H	8.25	9.80	8.60	8.80	8.80

The results from I. would agree better with the formula $C_{10}H_{18}O_5$; the increase in the percentage of both carbon and hydrogen, however, in II. and III. indicates that moisture was still being given off. *A priori* considerations also would make the formula $C_{10}H_{20}O_4$ more probable. This supposition was strengthened, as will be seen, by the composition of the silver salt. The sodium salt obtained from this acid was crystalline; the silver salt prepared from the sodium salt was obtained as a white flocculent precipitate, and when exposed for some time to light did not blacken. The dried salt when analysed gave the following results:

I. 0.1738 gram substance yielded 0.2452 gram $CO_2 = 0.06687$ gram C, and 0.0860 gram $H_2O = 0.00955$ gram H.

II. 0.2465 gram substance yielded 0.3415 gram $CO_2 = 0.09313$ gram C, and 0.1242 gram $H_2O = 0.01380$ gram H.

III. 0.2027 gram substance yielded 0.2818 gram $CO_2 = 0.07685$ gram C, and 0.1037 gram $H_2O = 0.01152$ gram H.

IV. 0.0760 gram substance yielded 0.0275 gram Ag.

V. 0.2061 gram substance yielded 0.0748 gram Ag.

	Calculated for		Found.				
	$C_{10}H_{17}O_5Ag$.	$C_{10}H_{19}O_4Ag$.	I.	II.	III.	IV.	V.
C	36.92	38.58	38.47	37.78	37.91	...	...
H	5.23	6.10	5.49	5.59	5.68	...	...
Ag	33.23	34.72	...	...	...	36.18	36.29

The solution of the ammonium salt of this acid, prepared by neutralising the acid with dilute ammonia, when evaporated on a water-bath gave off a rather toxic odor. The solution became viscid and brownish, and would not crystallise. A silver salt, however, was prepared which became only grayish on exposure to light, and of which two silver estimations were made:

I. 0.2205 gram substance yielded 0.0965 gram Ag = 43.76 per cent.

II. 0.1893 gram substance yielded 0.0835 gram Ag = 44.10 per cent.

Apparently the ammonia not only neutralises the acid, but also effects other changes which will require special study.

The aqueous acid liquid, resulting from the addition of dilute sulphuric acid to the solution of the potassium salts which remained after the separation of the oily acid layer, was also distilled with water vapor. The acid distillate was neutralised with sodium bicarbonate, the solution evaporated, and the residue extracted with hot absolute alcohol. Several crops of sodium salt were thus obtained, small yet handsome prisms resulting in one case. From one of these crops a silver salt was obtained as a white curdy precipitate, which soon darkened and, upon standing in the desiccator, underwent decomposition. The first silver estimation yielded 39.7 per cent. Ag, the second 43.9 per cent., and the third 62.2 per cent. This precipitate probably consisted of a mixture of the silver salt mentioned above, together with the silver salts of lower fatty acids, *e. g.* formic acid. This question, however, deserves to be further investigated, especially since in one of the earlier experiments a silver salt obtained in the same manner was analysed, with the following results:

I. 0.2745 gram substance yielded 0.3072 gram CO_2 = 0.08378 gram C, and 0.1100 gram H_2O = 0.01222 gram H.

II. 0.2425 gram substance yielded 0.2727 gram CO_2 = 0.07437 gram C, and 0.0990 gram H_2O = 0.0110 gram H.

III. 0.3020 gram substance yielded 0.1471 gram Ag.

	Calculated for			Found.		
	$C_5H_9O_2Ag$.[1]	$C_6H_{11}O_2Ag$.	$C_6H_{11}O_3Ag$.	I.	II.	III.
C	28.70	32.28	30.12	30.52	30.66	...
H	4.30	4.93	4.60	4.45	4.53	...
Ag	51.67	48.43	45.18	...	...	48.70

No satisfactory formula could be calculated from these results.

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[1] Semmler (Ber. d. chem. Ges. **24**, 209) states that the aldehyde $C_{10}H_{18}O$ from balm oil, when oxidised, yields isovaleric acid, and bases upon this fact his structural formula. He does not, however, furnish a single analytical proof.

The solubility of the non-volatile acid in water and ether suggested the treatment of the aqueous acid liquid with ether after the volatile products had been removed by distillation with water vapor. The separated ethereal layers, upon evaporation of the ether, yielded a reddish, viscid acid liquid which resembled that obtained from the original solution of the potassium salts upon the addition of sulphuric acid. Its ethereal solution does not decolorise bromine. It is precipitated from its aqueous solution by sodium acid sulphite, but apparently does not combine with this salt. No satisfactory results have thus far been obtained with phenyl-hydrazine or with benzoyl chloride. These experiments, however, are to be repeated with purer material as soon as this can be obtained, for it is necessary to ascertain the nature of the two additional oxygen atoms before the compound is oxidised any farther. That they are not present in the form of carboxyl oxygen is shown by the silver salt. *A priori* one would expect them to be present as hydroxy oxygen, two hydroxyl groups having been added in place of the double bond.

In conclusion I desire to render thanks to Messrs. Fritzsche Bros., who have kindly furnished the material for these investigations, which are by no means completed and will be continued.

PHARMACEUTICAL LABORATORY, UNIVERSITY OF WISCONSIN, *January*, 1892.

PROTEIDS OR ALBUMINOIDS OF THE OAT KERNEL.

SECOND PAPER.[1]

BY THOMAS B. OSBORNE.

In a paper on the proteids of the oat kernel, published in this journal,[2] the writer described a globulin obtained from the oat kernel by extraction with a 10-per cent. sodium chloride brine heated to 65° C. (Preparation **20**). It was shown that this globulin differs from that extracted by the same brine at 20° C. both in properties and composition, and that on cooling the warm saturated solution of this body in dilute sodium chloride brine, crystals were several times obtained—once in the form of rhombohedra and at other times in the form of octahedra.

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[1] Read at the meeting of the National Academy of Sciences in New York, Nov. 10, 1891. From advance sheets of the Report Conn. Agri. Expt. Station, 1891.

[2] This Journal **13**, 406; also Report Conn. Agri. Expt. Station, 1890.

This globulin has been further investigated, and the results obtained are the main subject of this paper.

PROTEID DERIVED FROM THE "ALBUMINATE."

Preparations "21," "22" *and* "23."

When the oat proteids brought into solution in cold brine[1] are precipitated by saturating the extract with ammonium sulphate, a considerable part of this precipitate is always found to have lost its solubility in the salt-solution by conversion into a form called by Weyl "an albuminate" (Preparations 15 and 16). In this state it is soluble in a 1-per cent. solution of sodium carbonate.

On treating ten pounds of freshly ground oats with brine, precipitating the filtered solution by saturating with ammonium sulphate, and extracting the precipitate thus obtained with brine, it was found that a very large part of the globulin originally dissolved was converted into the so-called "albuminate." After washing the latter thoroughly with brine to free it completely from the unchanged globulin, it was dissolved in a 1-per cent. sodium carbonate solution. About two-thirds of this solution was then treated with carbon dioxide for three hours, whereby a heavy white precipitate settled out. This precipitate was collected on a filter and allowed to drain overnight. The next morning it was found to have become transparent and gummy about the edges.

This precipitate was now completely soluble in salt-solution, and had all the properties of the globulin (20) previously obtained from the hot sodium chloride extract. The entire precipitate was then dissolved in 1 litre of brine and dialysed for four days, during which time all but a trace of the substance separated out. The proteid thus precipitated was seen under the microscope to consist of spheroids of about $\frac{1}{10}$ mm. diameter or less, similar to those obtained by cooling a warm solution of the globulin. After filtering off, washing with alcohol, ether and absolute alcohol, 21 grams of the air-dried material were obtained. This substance was completely soluble in brine, and was precipitated therefrom by diluting with water, by saturating with sodium chloride, or by adding minute quantities of hydrochloric, nitric or acetic acid. In the entire absence of salts, extremely small amounts of the acids just named dissolved the proteid instantly and completely, but the addition of a little sodium chloride precipitated it from this solution, the extent of the precipitation depending on the relative quantities of the acid and salt present. The precipitation was complete when certain proportions of salt and acid were used. Addition of strong soda-lye to the solution of the proteid in dilute acid gave a heavy precipitate which dissolved but slowly in excess of soda, although the final mixture contained over 25 per cent. of sodium hydrate. Addition of copper sulphate to this alkaline solution gave the biuret violet. With Millon's reagent and with nitric acid the usual proteid reactions were obtained. Alcohol containing a minute amount of free acid dissolved the substance completely. Its composition was found to be as follows:

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[1] Unless otherwise specified, "brine" and "salt-solution" are to be understood in this paper to signify aqueous solutions of very pure sodium chloride, containing 10 per cent. NaCl, used at common temperatures.

OAT PROTEID *derived from Sodium Carbonate Solution of the "Albuminate."—Preparation* **21.**

			Ash-free.	
	I.	II.	I.	II.
Carbon	52.28	..	52.30	..
Hydrogen	6.98	..	6.98	..
Nitrogen	17.86	17.73	17.86	17.73
Sulphur	0.69	..	0.69	..
Oxygen	..	..	22.17	..
Ash	0.03	..	..	..
			100.00	

Ash.—0.6759 gram substance, dried at 110° C., gave 0.0002 gram of ash = 0.03 per cent.

Carbon and hydrogen.—0.4610 gram dried substance gave 0.887 gram CO_2 = 52.28 per cent. C, and 0.3220 gram H_2O = 6.98 per cent. H.

Nitrogen, I (Dumas' method).—0.3474 gram dried substance gave 52.15 cc. N at 13° C. (barometer 768.2 mm. at 23° C.) = 17.86 per cent. N.

II (Kjeldahl method).—1.0108 grams dried substance gave ammonia = 21.8 cc. HCl sol. (1 cc. = 0.00822 gram N) = 17.73 per cent. N.

Sulphur.—0.7695 gram dried substance gave 0.0380 gram $BaSO_4$ = 0.0052 gram S = 0.69 per cent.

In all respects save one, this substance behaved exactly like the globulin obtained by extracting ground oats with hot sodium chloride solution. The latter proteid dissolved to a turbid solution in cold, and to a perfectly clear solution in hot distilled water. So far as the usual methods of analysis show, the two bodies are identical in composition, as is seen from the following figures:

	Globulin extracted from oats by hot sodium chloride solution —average of two analyses. Preparation 20.	Globulin derived from sodium carbonate solution of "albuminate." Preparation 21.
Carbon	52.22	52.30
Hydrogen	6.98	6.98
Nitrogen	17.82	17.86
Sulphur	0.77	0.79
Oxygen	22.21	22.17
	100.00	100.00
Ash	0.19	0.03

Another preparation of this substance was made by dissolving a second portion of the "albuminate" in 2-per cent. sodium carbonate solution, precipitating with carbon dioxide, washing thoroughly with water, dissolving in brine and diluting the solution with a large amount of water. The final, snow-white precipitate was filtered off and, after washing with alcohol and ether, weighed eleven grams. Its properties are exactly the same as those of **21**, except that it is slightly soluble in hot distilled water. Its composition, as determined by analysis, here follows :

OAT PROTEID *derived from Sodium Carbonate Solution of the "Albuminate."—Preparation* **22.**

		Ash-free.
Carbon	51.98	52.05
Hydrogen	6.92	6.93
Nitrogen	17.83	17.85
Sulphur } Oxygen }	..	23.17
Ash	.13	..
		100.00

Ash.—0.5437 gram substance, dried at 110° C., gave 0.0007 gram ash = 0.13 per cent.

Carbon and hydrogen.—0.5789 gram dried substance gave 1.1030 grams CO_2 = 51.98 per cent. C, and 0.3609 gram H_2O = 6.92 per cent. H.

Nitrogen.—0.4230 gram dried substance gave 63 cc. N at 13° C. (barometer 773 mm. at 23° C.) = 17.83 per cent. N.

The filtrate from the precipitate produced by carbon dioxide in the preparation of the preceding substance (**22**) was diluted with an equal volume of water, further treated with carbon dioxide for about three hours and allowed to stand overnight. The resulting precipitate was filtered off and washed with water, alcohol and ether. 5 grams of substance having the same properties as Preparations **21** and **22** were thus obtained. Analysis of this product gave the following results:

OAT PROTEID *derived from Sodium Carbonate Solution of the "Albuminate."—Preparation* 23.

		Ash-free.
Carbon	52.16	52.35
Hydrogen	7.00	7.02
Nitrogen	17.68	17.73
Sulphur	0.73	0.73
Oxygen	..	22.17
Ash	0.36	..
		100.00

Ash.—0.5500 gram substance, dried at 110° C., gave 0.0020 gram ash = 0.36 per cent.

Carbon and hydrogen.—0.4388 gram dried substance gave 0.8393 gram CO_2 = 52.16 per cent. C, and 0.2766 gram H_2O = 7.00 per cent. H.

Nitrogen.—0.3659 gram dried substance gave 54.36 cc. N at 13° C. (barometer 767.6 mm. at 22° C.) = 17.68 per cent. N.

Sulphur.—0.9135 gram dried substance gave 0.0484 gram $BaSO_4$ = 0.0066 gram S = 0.73 per cent. S.

Crystallisation of the Globulin obtained from the so-called "Albuminate."

300 cc. of 1-per cent. sodium chloride solution were heated to 70° C. with 5 grams, *i. e.* an excess of Preparation **21**, and filtered on a steam-jacketed funnel. On cooling, the filtrate rapidly deposited a large crop of rhombohedral crystals. The residue undissolved by the hot 1-per cent. brine was washed with the same weak brine heated to 70°. On cooling, the washings deposited octahedral crystals. This process was repeated several times with other portions of Preparation **21**. In most cases the filtrate deposited rhombohedral and the washings octahedral crystals. The residues which had been filtered out were, as far as possible, dissolved and crystallised from 1-per cent. brine, yielding either octahedral crystals or mixtures of octahedra and rhombohedra. The different crops of crystals were collected on separate filters, according as they were wholly rhombohedra or octahedra or mixtures of the two. Three preparations, "**24**," "**25**" and "**26**," were obtained in this way, and these were as

usual washed with water, alcohol and ether, and dried at 110° for analysis. Thus prepared they retained their crystalline form entirely unchanged, and had in all respects the same properties as the mother-substance (**21**).

Prof. S. L. Penfield kindly examined these crystals, and states that they appear to be rhombohedra and octahedra, athough the former have no action on polarised light. He suggests that the apparent rhombohedra may be octahedra with but six faces developed, such crystals occurring in nature. As they are too small for measurement (less than $\frac{1}{10}$ mm. long), this point cannot be definitely determined. Analyses of the three preparations gave the following percentages :

CRYSTALLISED OAT GLOBULIN *derived from* **21**.
Preparation **24**.

		Ash-free.
Carbon	52.14	52.17
Hydrogen	6.96	6.96
Nitrogen	17.92	17.93
Sulphur	0.53	0.53
Oxygen	..	22.41
Ash	0.06	..
		100.00

Ash.—0.4600 gram substance, dried at 110° C., gave 0.0003 gram ash = 0.06 per cent.

Carbon and hydrogen.—0.4463 gram dried substance gave 0.8835 gram CO_2 = 52.14 per cent. C, and 0.2795 gram H_2O = 6.96 per cent. H.

Nitrogen.—0.4042 gram dried substance gave 63.0 cc. N at 17° C. (barometer 756.3 mm. at 21° C.) = 17.92 per cent. N.

Sulphur.—0.6345 gram dried substance gave 0.0242 gram $BaSO_4$ = 0.0033 gram S = 0.53 per cent.

CRYSTALLISED OAT GLOBULIN *derived from* **21**.
Preparation **25**.

		Ash-free.
Carbon	52.00	52.11
Hydrogen	7.09	7.10
Nitrogen	17.91	17.94
Sulphur } Oxygen }	..	22.85
Ash	0.20	..
		100.00

Ash.—0.2035 gram substance, dried at 110°, gave 0.0004 gram ash = 0.20 per cent.

Carbon and hydrogen.—0.2562 gram dried substance gave 0.4885 gram CO_2 = 52.00 per cent. C, and 0.1635 gram H_2O = 7.09 per cent. H.

Nitrogen.—0.3935 gram dried substance gave 61.3 cc. N at 17° C., (barometer 756.5 mm. at 21° C.), = 17.91 per cent. N.

Crystallised Oat Globulin *derived from* **21.**
Preparation **26.**

		Ash-free.
Carbon	52.23	52.25
Hydrogen	7.08	7.08
Nitrogen	17.81	17.82
Sulphur	0.52	0.52
Oxygen	..	22.33
Ash	0.05	..
		100.00

Ash.—0.3974 gram substance, dried at 110° C., gave 0.0002 gram ash = 0.05 per cent.

Carbon and hydrogen.—0.2866 gram dried substance gave 0.5489 gram CO_2 = 52.23 per cent. C, and 0.1828 gram H_2O = 7.08 per cent. H.

Nitrogen.—0.3123 gram dried substance gave 48.31 cc. N at 17° C. (barometer 757 mm. at 21° C.) = 17.82 per cent. N.

Sulphur.—0.3598 gram dried substance gave 0.0135 gram $BaSO_4$ = 0.0018 gram S = 0.52 per cent.

Crystallised Oat Globulin *derived from* **21.**

	24.—Rhombohedra.	**25.**—Rhombohedra and Octahedra.	**26.**—Octahedra.
Carbon	52.17	52.11	52.25
Hydrogen	6.96	7.10	7.08
Nitrogen	17.93	17.94	17.82
Sulphur	0.53	22.85	0.52
Oxygen	22.41		22.33
	100.00	100.00	100.00
Ash	0.06	0.20	0.05

No chlorine could be detected in these crystals. It is thus shown that the crystallised globulin, except for its slightly lower content of sulphur, has the same composition as the mother-substance, and agrees in all respects with the globulin obtained directly from ground oats by extraction with hot salt-solution and described in my former paper, except that it is not soluble in water and contains a little less sulphur.

It is further to be noted that the methods of preparation rendered possible the fractional separation of the substance into its component parts, had it been a mixture of two or more globulins. It seems improbable that the sodium chloride which Grübler found in his crystallised globulin from squash-seed was anything more than an accidental impurity. The ash of Grübler's preparations contained traces of the various salts present in the solutions from which they separated, and there appears to be no good ground for Grübler's assumption that the crystallised proteids are definite compounds of globulin with sodium chloride or with other inorganic bodies, since the content of total mineral matters is variable and, as in my preparations 24 and 26, sometimes amounts to but 0.05 per cent. of the proteid.

Globulin obtained by Direct Extraction of Ground Oats with Sodium Carbonate Solution.

100 grams of ground oats were digested with a 1-per cent. sodium carbonate solution, the extract was filtered clear, and the sodium carbonate converted into bicarbonate by treatment with carbon dioxide. The solution was then saturated with ammonium sulphate and the heavy precipitate filtered off. This precipitate was washed with a saturated solution of ammonium sulphate until the washings no longer reacted alkaline. The precipitate was then thoroughly extracted with salt solution and this extract dialysed. After the removal of the salts by dialysis, the proteid which had separated was filtered off and washed with alcohol and ether. It weighed, air-dry, 1.5 grams, being therefore about 1.5 per cent. of the oat kernel. Dried at 110° for analysis, it was found to have the following composition:

OAT PROTEID *extracted from Ground Oats by Sodium Carbonate Solution, and Soluble in Sodium Chloride Solution.*
Preparation 27.

			Ash-free.	
	I.	II.	I.	II.
Carbon	51.68	..	51.82	..
Hydrogen	6.91	..	6.93	..
Nitrogen	17.92	17.91	17.95	17.94
Sulphur } Oxygen }	..	..	23.30	..
Ash	0.26	..	..	..
			100.00	

Ash.—0.2652 gram substance, dried at 110° C., gave 0.0007 gram ash = 0.26 per cent.

Carbon and hydrogen.—0.2296 gram dried substance gave 0.4350 gram $CO_2 = 51.68$ per cent. C, and 0.1429 gram $H_2O = 6.91$ per cent. H.

Nitrogen, I.—0.3441 gram dried substance gave 52.15 cc. N at 13° C. (barometer 764.0 mm. at 25° C.) = 17.92 per cent. N.

Nitrogen, II.—0.3294 gram dried substance gave 50.14 cc. N at 14° C. (barometer 762.0 mm. at 23° C.) = 17.91 per cent. N.

Summary of Analyses of Oat Globulin.

The agreement of the analyses of the eight different preparations of oat globulin may be seen from the following table:

	20.	**21.**	**22.**	**23.**
Carbon	52.22	52.30	52.05	52.35
Hydrogen	6.98	6.98	6.93	7.02
Nitrogen	17.82	17.86	17.85	17.73
Sulphur	0.77	0.69	23.17	0.73
Oxygen	22.22	22.17		22.17
	100.00	100.00	100.00	100.00

	24.	**25.**	**26.**	**27.**
Carbon	52.17	52.11	52.25	51.82
Hydrogen	6.96	7.10	7.08	6.93
Nitrogen	17.93	17.94	17.82	17.95
Sulphur	0.53	22.85	0.52	23.30
Oxygen	22.41		22.33	
	100.00	100.00	100.00	100.00

The writer has nowhere found any description of a vegetable proteid like this. Although its proportion of carbon is the same as that of the globulin extracted from oats by cold salt-solution, its nitrogen-content is 1 per cent. greater. It contains nearly 1 per cent. less of nitrogen, about ½ per cent. more of carbon, and but ½ as much sulphur, as Chittenden and Hartwell[1] found in the globulin or "vegetable vitellin" of squash-seed.

Barbieri's analysis of squash-seed globulin agrees fairly well with these analyses of the crystallised oat globulin, but carbon and sulphur are somewhat lower, nitrogen high, and as regards sulphur and nitrogen his analysis differs materially from the later ones of Chittenden and Hartwell.

Grübler's earlier analyses of squash-seed globulin, which gave 53.21 per cent. of carbon and 19.22 per cent. of nitrogen, were evidently incorrect, and in a recent publication[1] this chemist states the composition of crystallised proteid from squash-seed as given below, where the various analyses of vegetable globulin, except this earlier one of Grübler's, are tabulated.

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[1] J. Physiol **11**, 437-440.

I have obtained from flax-seed a crystallised globulin whose composition agrees quite nearly with that of squash-seed vitellin.

Composition of Vegetable Globulin.

	Ritthausen.		Barbieri.	Ritth.	Chittenden and Hartwell.			Grübler.	Osborne.	
	Hemp.	Castor Bean.	Squash-seed.						Flax Seed.	Oats.
	Cryst.	Cryst.	Amorph	Cryst.	Cryst.	Spheroid	Amorph.	Cryst.	Cryst.	Cryst.
C	50.98	50.88	51.88	51.61	51.60	52.03	51.81	51.48	51.41	52.18
H	6.92	6.98	7.51	7.00	6.97	6.93	6.94	6.76	6.96	7.05
N	18.73	18.58	18.08	..	18.80	19.08	18.71	18.14	18.58	17.90
S	0.82	0.77	0.60	.	1.01	1.04	1.01	0.96	0.79	0.53
O	22.55	22.79	21.93	..	21.62	20.92	21.53	22.66	22.26	22.34
	100.00	100.00	100.00		100.00	100.00	100.00	100.00	100.00	100.00
Ash			1.11		0.30	0.36		0.18		0.10

Proteid extracted from Ground Oats by Direct Treatment with Alkali Carbonates.

The precipitate produced by saturating with ammonium sulphate the sodium carbonate extract of the oats from which the globulin 27 had been separated, was next washed with warm 80-per cent. alcohol until all the proteid soluble in that liquid was removed. The residue was then found to be quite insoluble in 1-per cent. sodium carbonate solution and was therefore treated with $\frac{2}{10}$-per cent. caustic potash solution, filtered, and the dissolved proteid completely precipitated by neutralising with dilute acetic acid. After washing this substance with water, alcohol and ether, and drying at 110°, its composition was as follows:

OAT PROTEID *extracted from Ground Oats by Sodium Carbonate Solution.—Preparation* 28.

			Ash-free.	
	I.	II.	I.	II.
Carbon	53.25	..	53.63	..
Hydrogen	7.13	..	7.18	..
Nitrogen	15.99	15.89	16.11	16.01
Sulphur	0.81	..	0.82	..
Oxygen	..	..	22.26	..
Ash	0.72	..	..	..
			100.00	

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[2] J. prakt. Chem. 44, 369.

Ash.—0.5661 gram substance, dried at 110° C., gave 0.0041 gram ash = 0.72 per cent.

Carbon and hydrogen.—0.3269 gram dried substance gave 0.6383 gram CO_2 = 53.25 per cent. C, and 0.2096 gram H_2O = 7.13 per cent. H.

Nitrogen, I.—0.3637 gram dried substance gave 49.33 cc. N at 13° C. (barometer 761.5 mm. at 25° C.) = 15.99 per cent. N.

Nitrogen, II.—0.3916 gram dried substance gave 52.95 cc. N at 13° C. (barometer 759.2 mm. at 23° C.) = 15.89 per cent. N.

Sulphur.—0.5000 gram dried substance gave 0.0295 gram $BaSO_4$ = 0.0041 gram S = 0.81 per cent. S.

If this analysis is compared with that of Preparation **17**, which was obtained from ground oats by direct extraction with $\frac{2}{10}$-per cent. potash solution, it will be seen that the two agree closely.

	28.	17.
Carbon	53.63	53.49
Hydrogen	7.18	7.01
Nitrogen	16.11	16.39
Sulphur	0.81	0.99
Oxygen	22.27	22.12
	100.00	100.00
Ash	0.72	1.00

These two bodies are thus shown to be essentially the same in composition, and the results of direct extraction with alkili as given in my first paper are confirmed.

CONCLUSION.

The proteids of the oat kernel undergo great change in contact with water or sodium chloride solution. The body extracted by direct treatment of ground oats with alcohol differs much in properties and composition from that extracted by alcohol after the ground oats have for some time had contact with water or sodium chloride solution.

Direct treatment with sodium carbonate solution yields the same globulin as that obtained by direct treatment with hot sodium chloride solution, but differing from that obtained by direct treatment with cold sodium chloride solution. Sodium carbonate solution also extracts another proteid—the same as that yielded by direct extraction with dilute potash-lye—which, again, is distinct in composition from that obtained after the oats have been in contact with water. It is remarkable that all these transformations are the result of the use of water or salt-solution as contrasted with the use of alcohol, alkali or heat: three agents known to suspend or destroy ferment action.

The fact that the globulin extracted after treatment of the ground oats with alcohol has the same composition as that obtained by direct treatment with sodium chloride, would indicate that alcohol temporarily suspends a ferment-action which is induced by water or solutions of neutral salts.

It is probable that the primary proteids originally contained in the oat kernel are the three following bodies:

PRIMARY OAT PROTEIDS.

	Alcohol-soluble Proteid—Average of five analyses.	Salt-soluble Proteid or Globulin—Average of nine analyses.	Alkali-soluble Proteid—Average of two analyses.
Carbon	53.01	52.19	53.56
Hydrogen	6.91	7.00	7.09
Nitrogen	16.43	17.86	16.20
Sulphur	2.26	0.65	0.90
Oxygen	21.39	22.30	22.25
	100.00	100.00	100.00

Of the above substances the alcohol-soluble proteid forms about 1.25 per cent., the globulin about 1.5 per cent., and the alkali-soluble body the remainder of the proteids contained in the oat kernel, with the possible exception of extremely small amounts of proteose and acid-albumin. The latter two substances are quite probably the results of change occurring during extraction; the evidence, however, on this point is not conclusive.

Three other proteids are obtained—evidently by the alteration of the primary proteids, and probably through ferment-action—if the ground oats are subjected to contact with water or solutions of neutral salts. The composition of these derived or secondary proteids is as follows:

SECONDARY OAT PROTEIDS.

	Alcohol-soluble Proteid—Average of four analyses.	Salt-soluble Proteid or Globulin—Average of four analyses.	Alkali-soluble Proteid—Average of two analyses.
Carbon	53.70	52.34	52.49
Hydrogen	7.00	7.21	7.10
Nitrogen	15.71	16.88	17.11
Sulphur	1.78	0.88	0.80
Oxygen	21.83	22.69	22.50
	100.00	100.00	100.00

It would appear that none of the proteids from the oat kernel have hitherto been obtained and analysed in a state of purity. The author therefore reserves the right to revise the nomenclature of these bodies after further progress in his researches on the other vegetable proteids with which he is now engaged.

Laboratory of the Connecticut Agricultural Experiment Station, New Haven, Conn., *November*, 1891.

EUPATORIN: THE ACTIVE PRINCIPLE OF *EUPATORIUM PERFOLIATUM.*

By C. H. Shamel.

The dried *eupatorium perfoliatum*, gathered at blooming-time, was extracted by hot alcohol in a continuous extraction-apparatus for several hours. The excess of alcohol was distilled off and the thick residue treated with water acidulated with hydrochloric acid. A black gummy mass separated, which was removed by filtration, the filtrate neutralised with sodium carbonate and extracted with ether. On evaporation of the ether the active principle was deposited, either as a yellow resinous mass or as a yellow powder, which, on examination under the microscope, was found to consist of globular masses of needle-shaped crystals. The crystalline variety was analysed for nitrogen, but was found to contain none. The principle, in both the amorphous and crystalline forms, was insoluble in water, in concentrated sulphuric acid and in concentrated hydrochloric acid, but was soluble in even dilute nitric acid with a light-brown coloration. The nitric-acid solution, when allowed to evaporate spontaneously or in a vacuum over lime, crystallises in beautiful prisms and six-sided plates.

An aqueous solution of these crystals injected into mice killed them in a few hours. The crystals, when taken into the mouth, have first an acid taste from the nitric acid they contain, followed by a very bitter taste. The aqueous solution has only the bitter taste.

Chemical Characteristics.

The crystals of the nitrate are easily soluble in water and melt at 102°–103°. The principle itself does not melt, but at 250° suffers partial decomposition.

The solution of the nitrate was tested with the common alkaloid reagents, but gave the following reactions only: Phospho-molybdic acid, a green color; picric acid, a few needle-shaped crystals; auric chloride, colored slightly.

The principle is soluble in the alkalies. The solution in sodium hydroxide gave the following reactions, parallel tests being made with the sodium hydroxide solution alone: Phospho-molybdic acid, an instantaneous brilliant green coloration which soon fades; auric chloride, a black flocculent precipitate; picric acid, a deep-red coloration.

The ultimate analysis of the crystallised nitrate deprived of its water of crystallisation gave the following figures:

C	H	O	N
25.7 per cent.	3.1 per cent.	64.2 per cent.	1.55 per cent.
26.2	2.7	64.1	1.6

Or calculating the N as HNO_3, we have $HNO_3 \begin{cases} 6.97 \text{ per cent.} \\ 7.20 \end{cases}$

These figures would indicate that the formula is $C_{20}H_{25}O_{36}.HNO_3$, which would require the following as the theoretical composition:

C—26.49 per cent. H—2.76 per cent. O—64 per cent.
N—1.54 per cent. = HNO_3—6.96 per cent.

DI-BENZYLCARBINAMINE AND ITS CONDUCT TOWARD NITROUS ACID.

By W. A. Noyes.

Some time since Bamberger discovered several representatives of a new class of amines, to which he has given the name of "alicyclic."[1] The structural characteristic of this class of bases is that the amine group is combined with a carbon atom which forms a part of a hydrogenated benzene nucleus. Those prepared by Bamberger have been derivatives of naphthalin.[1] Bornyl amine[2] and hexamethylene diamine[3] show similar properties. It is probable that the menthyl amine recently prepared by Wallach[4] will show a similar conduct, but a full description of the body has not been published.

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[1] Ber. d. chem. Ges. **22**, 769.

As regards their chemical character, the alicyclic amines are strong bases; their carbonates are precipitated from ethereal solutions of the bases by moist carbon dioxide, are stable salts, and have a strongly alkaline reaction; the free bases combine directly with carbon disulphide at ordinary temperatures, forming sulphocarbamates; and the nitrites are stable and do not decompose even in boiling water. In this last respect, especially, the alicyclic amines differ from all other amines at present known.

The conduct of these amines suggests the question whether their peculiar behavior is characteristic only of alicyclic bases, or whether possibly other amines might be found which would show similar properties. The facts that naphthobenzyl amine forms a nitrite which is stable at low temperatures,[5] and that di-iso-propylamine forms a nitrite which is converted into a nitroso compound only by long boiling with water,[6] indicate that aliphatic bases may, in some cases, be comparatively stable toward nitrous acid. It seemed possible that a base containing the amine group connected with the central carbon atom in a somewhat large carbon complex, might show a similar conduct to that of an amine group connected with a hydrogenated benzene nucleus. In order to test this question, di-benzylcarbinamine has been prepared and its character studied.

The base was obtained by the reduction of di-benzylketoxim by means of sodium and absolute alcohol. A hot solution of 13.5 grams of the ketoxim in 100 cc. of absolute alcohol was poured slowly into a flask connected with an inverted condenser and containing 20 grams of sodium. When the reaction slackened the flask was heated with a low flame, and alcohol was added in portions of 25 cc. at a time whenever a crust of sodium ethylate appeared on the sodium. When the sodium had disappeared, the alcohol and a part of the base were distilled in a current of steam. It was found, however, that the base is very difficultly volatile even with superheated steam, and also that some of the unchanged oxim passed over, so that the pure base could not be separated by this method. The following method was found more satisfactory After distilling off the alcohol with a current of steam the alkaline solution was diluted slightly and allowed to cool. The base is almost insoluble in water and separates, together with some unchanged oxim, as an oily liquid. The liquid was separated from the alkaline solution by filtration or by means of a little ether, and the base was converted into the chloride by treatment with dilute hydrochloric acid. The solution was then rendered slightly alkaline with caustic soda, and then acid with acetic acid. After standing for some time the oxim separates almost completely, and can be removed from the solution by filtration. Caustic soda will then precipitate the base from the filtrate in a nearly pure condition. It can be further purified by conversion into the chloride and recrystallisation of the salt from water.

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[1] Ber. d. chem. Ges. **20**, 2915; **21**, 847, 1112, 1786, 1892; **22**, 625, 767, 777, 943, 1295, 1311, 1374, 1760; **23**, 291, 876.

[2] Ibid. **21**, 1126.

[3] Ibid. **22**, 2172.

[4] Ibid. **24**, 3992.

[5] Ibid. **21**, 257.

[6] Rec. trav. Chim. **8**, 207. See also Ber. d. chem. Ges. **22**, Ref. 343.

Di-benzylcarbinamine.

The free base separates in oily drops when caustic soda is added to a solution of one of its salts. After some time the drops solidify to a crystalline mass, a transformation which can be much hastened by the addition of some small particles of the solid base.

After drying over sulphuric acid the base melts at 47° and boils without decomposition at 330°. The base dissolves readily in alcohol, ether and ligroin, but is nearly insoluble in water. It is not hygroscopic. It shows a strongly alkaline reaction with test papers. The analyses gave the following results:

I. 0.1874 gram of the base gave 0.5851 gram CO_2 and 0.1328 gram H_2O.

II. 0.2198 gram of the base gave 0.6854 gram CO_2 and 0.1589 gram H_2O.

	Calculated for $\begin{matrix}C_6H_5CH_2\\C_6H_5CH_2\end{matrix}>CHNH_2$.	Found.	
		I.	II.
C_{15}	85.31	85.17	85.05
H_{17}	8.06	7.87	8.03
N	6.63	...	...

The chloride, $C_{15}H_{15}NH_2HCl$, separates in compact crystals, which group themselves in warty aggregates on the bottom of the crystallising dish. The salt is moderately soluble in water. It melts sharply at 205°.

0.1936 gram of the salt gave 0.1113 gram of AgCl.

	Calculated.	Found.
Cl	14.34	14.22

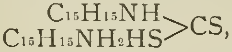
The chloroplatinate, $(C_{15}H_{15}NH_3)_2PtCl_6$, is precipitated in fine crystalline scales having a light-yellow color when chloroplatinic acid is added to a solution of the chloride of the base. The salt may be recrystallised from hot water without decomposition.

0.2215 gram of the salt gave 0.0514 gram Pt.

	Calculated.	Found.
Pt	23.44	23.21

The nitrite, $C_{15}H_{15}NH_2HNO_2$, is precipitated in fine needles which form a compact, cotton-like mass when a solution of sodium or potassium nitrite is added to a concentrated solution of the chloride. After filtering off and drying over sulphuric acid, a weighed portion of the salt was dissolved in water and a known part of the very dilute solution was treated with hydrochloric acid, sulphanilic acid and naphthylamine chloride. A standard solution of sodium nitrite containing the amount of nitrous acid calculated to correspond to the solution containing the nitrite of the base was treated with the same reagents, and the colors were compared. No difference could be detected in the tints.

At ordinary temperatures solutions of the nitrite appear to be perfectly stable, and there is no difficulty in obtaining the salt in pure condition. Dilute solutions may be boiled for some time with very slight decomposition, as was proved by quantitative color reactions. When, however, a concentrated solution of the nitrite is heated to the boiling point, nitrogen is evolved and di-benzyl carbinol is formed as the chief product of the decomposition. The details are given below.

Di-benzylcarbinamine sulphocarbamate of di-benzylcarbinamine,

$\begin{matrix} C_{15}H_{15}NH \\ C_{15}H_{15}NH_2HS \end{matrix} > CS$, is formed when di-benzylcarbinamine is added to carbon di-sulphide. The base dissolves completely at first, but in a moment the salt begins to separate and soon fills the liquid with an almost solid mass of very fine crystals. These were filtered off, washed with carbon disulphide and allowed to dry in the air. The substance melts at 141°–143°. At the same time it decomposes and hydrogen sulphide is evolved,

probably with the formation of a thio-urea, $\begin{matrix}C_{15}H_{15}NH\\C_{15}H_{15}NH\end{matrix}>CS$. The analysis of the salt gave the following result:

0.0924 gram of the substance gave 0.0870 gram $BaSO_4$ (Carius).

	Calculated for $\begin{matrix}C_{15}H_{15}NH\\C_{15}H_{15}NH_2HS\end{matrix}>CS$.	Found.
S	12.85	12.94

Di-benzylcarbinol.

To obtain the substance formed by the decomposition of the nitrite of di-benzylcarbinamine, 5.8 grams of the chloride of the base were dissolved in about 30 cc. of water, and a strong solution of sodium nitrite containing 1.62 grams of the salt was added. The solution was then heated overnight on the water-bath. The product of the decomposition which separated as an oil, heavier than water, was taken up with a small amount of ether; the ethereal solution was dried with potassium carbonate and was then distilled. The product distilled mainly at 320°–325°. The analysis of a portion of the distillate indicated that it consisted of a mixture of di-benzylcarbinol and of the hydrocarbon which would be obtained from the alcohol by the loss of one molecule of water.

0.2754 gram of the liquid gave 0.8830 gram CO_2 and 0.1844 gram H_2O.

	Calculated for $\begin{matrix}C_6H_5CH_2\\C_6H_5CH_2\end{matrix}>CHOH$.	Found.	Calculated for $\begin{matrix}C_6H_5CH_2\diagdown\\C_6H_5CH\;/\!\!/\end{matrix}CH$.
C	84.90	87.48	92.78
H	7.55	7.44	7.22

Thinking that decomposition might have taken place during the distillation, a fresh solution of the chloride of the base was taken, the equivalent amount of sodium nitrite was added, and the solution was heated for a short time on the water-bath. The oil which separated was washed with water and dried over sulphuric acid in a vacuum. Two different specimens of the alcohol prepared in this way were analysed. The specimen used for the second and third analyses was heated on the water-bath for a shorter time than that used for the first analysis. The results of the analyses indicate that di-benzylcarbinol is the chief product of the decomposition of the nitrite, but that a small amount of some substance richer in carbon, probably an unsaturated hydrocarbon, is formed.

I. 0.1283 gram of the oil gave 0.4020 gram CO_2 and 0.0841 gram H_2O.

II. 0.1756 gram gave 0.5511 gram CO_2 and 0.1180 gram H_2O.

III. 0.1336 gram gave 0.4188 gram CO_2 and 0.0752 gram H_2O.

	Calculated for $\begin{matrix}C_6H_5CH_2\\C_6H_5CH_2\end{matrix}>CHOH$.	Found.		
		I.	II.	III.
C	84.90	86.08	85.59	85.49
H	7.55	7.28	7.47	7.52

Di-benzylcarbinol, when prepared as described, is a viscous liquid, heavier than water and having a slight yellow color, probably due to impurities. The boiling point is probably between 320° and 325°, but the determination cannot be considered as accurate. Freund and Shönfeld[1] have recently shown that the nitrite of a nonyl-amine gives by its decomposition a tertiary alcohol, instead of the primary alcohol which would be expected. To determine whether a similar change had taken place in the present case, a small quantity of the di-benzylcarbinol was dissolved in glacial acetic acid, and an excess of a cold solution of chromic acid in acetic acid was added. After standing for a few minutes the solution was diluted with water, and the oil which separated was taken up with ether. The ethereal solution was shaken with caustic soda to remove acetic acid and then evaporated to dryness. The oily residue was dissolved in alcohol, hydroxylamine chloride and caustic soda were added, and the solution was heated on the water-bath for half an hour. The oxim which was precipitated on pouring the solution into water was dried over sulphuric acid and recrystallised from ligroin. It separated in short white needles, identical in appearance with those of the oxim of di-benzylketone, and melting at the same temperature, 121°. Rattner[2] gives the melting point as 119.5°. The substance formed by the decomposition of di-benzylcarbinamine nitrite is, therefore, di-benzylcarbinol and not an isomer.

It appears from the experiments which have been described that the nitrite of di-benzylcarbinamine is more stable than the nitrites of most aliphatic amines. It does not, however, have the same stability as the nitrites of the "alicyclic" amines, and the latter form a class distinct in their properties from all other amines at present known.

ROSE POLYTECHNIC INSTITUTE, *March*, 1892.

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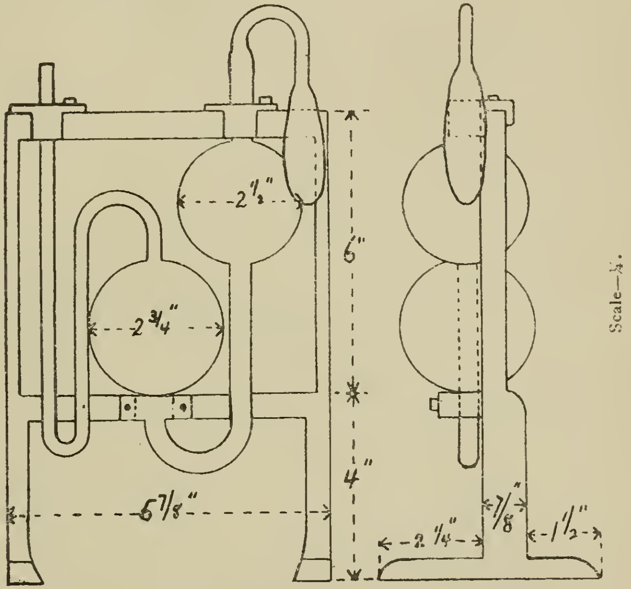
[1] Ber. d. chem. Ges. **21**, 3359.

[2] Ibid. **21**, 1317.

AN IMPROVED PIPETTE FOR GAS ABSORPTIONS.[1]

By Augustus H. Gill.

The writer has replaced the cumbersome "compound" pipette of Hempel by the "simple" one, fitted with a rubber bag after the manner of the pipettes in the Orsat gas apparatus, as furnished by Muencke. This has been found to preserve the reagents better and to possess the additional advantage of being much more easily refilled and handled.



The capillary is made of "white laid" glass, similar to that used for thermometers, and does away with the milk-glass tablet which is usually inlaid behind this part. To prevent the rubber connectors from slipping off, the end of the capillary is ground rough. A cast-iron stand is the mounting of the pipette, its tubes passing through movable brass pieces, and being held fast by filling in the annular space with a molten mixture of equal parts of rosin and beeswax; rubber tubing or cork can also be used for this filling. These stands admit of almost any size of pipette being used and of its easy replacement in case of breakage.

The apparatus was made for me most satisfactorily by Mr. Albert Hetschel, 33 Woodville Street, Boston.

Laboratory of Gas Analysis, Mass. Institute of Technology, Boston.

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[1] The apparatus can be obtained from Emil Greiner, New York.

Contributions from the Chemical Laboratory of Cornell University.

XVIII.—ON THE COPPER SULPHITES.

By Spencer B. Newbury.

In the course of an extended investigation of the compounds of copper and silver—undertaken in the hope of throwing some light on the peculiar differences which these two elements present, though belonging to the same family in the periodic system—the author's attention was called to the peculiar action of sulphur dioxide upon copper salts, and a series of experiments were made which have yielded interesting results, though somewhat aside from the purpose of the original investigation.

Cupric sulphite appears never to have been prepared. According to Musspratt,[1] cupric hydroxide is dissolved by a solution of sulphur dioxide to a green liquid which perhaps contains cupric sulphite; on standing or warming, a red crystalline salt is precipitated; this was supposed to be cuprous sulphite, but Rammelsberg proved it to be a cuproso-cupric sulphite, $CuSO_3.Cu_2SO_3.2H_2O$. By the action of sulphur dioxide on a mixed solution of cupric sulphate and ammonium sulphite, white leaflets of ammonium-cuprous sulphite were obtained by Rogojski and others, and by further action of sulphur dioxide this substance is converted into cuprous sulphite, $Cu_2SO_3.H_2O$. This compound forms red crystals, and closely resembles the cuproso-cuprous sulphite mentioned above. By the action of sulphur dioxide on a solution of cupric acetate, Etard[2] obtained cuprous sulphite in another form, *i. e.* in white crystalline leaflets; the red sulphite obtained by Rogojski is claimed by Etard to be a polymeric form of the same substance.

Action of sulphur dioxide on copper sulphate in presence of copper.—The formation of the cuproso-cupric sulphite by the action of sulphur dioxide on cupric hydroxide is evidently due to partial reduction of the cupric sulphite first formed:

$$3CuSO_3 + SO_2 + H_2O = CuSO_3.Cu_2SO_3 + H_2SO_4.$$

It appeared probable to the author that, if the above constitution of this salt is correct, it should be formed by the action of sulphur dioxide on copper sulphate solution in presence of metallic copper. This was found to be the case. A roll of thin sheet copper was placed in a ten-per cent. solution of copper sulphate, and a slow current of sulphur dioxide passed in for several hours. The copper soon became covered with a coating of red crystals, and the solution became at last almost completely decolorised. The crystals showed the characteristic form of the red salt. A determination of copper gave the following result:

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[1] Ann. Chem. (Liebig) **50**, 284.

[2] Compt. rend. **95**, 36, 137.

	Calculated for $CuSO_3.Cu_2SO_3.2H_2O$.	Found	
Cu	49.25	49.40	49.26

The loss of weight of the copper used was found to be about one-third of the copper contained in the salt: wt. of salt, 5.5676 grams; loss in wt. of copper, 1.0616 grams. From this it would appear that cupric sulphite is formed by the action of the sulphur dioxide on the copper sulphate, and that this is converted by the copper into cuproso-cupric sulphite: $2CuSO_3 + Cu = CuSO_3.Cu_2SO_3$. As the latter is constantly removed from the solution, the action of the sulphur dioxide continues until the decomposition of the sulphate is nearly complete. A large amount of sulphuric acid is, however, produced in the solution, and this brings about finally a condition of equilibrium beyond which point the action of the sulphur dioxide ceases.

Action of sulphur dioxide on cupric hydroxide.—It appeared to the author to be of interest to determine whether, in dissolving cupric hydroxide in sulphur dioxide solution, the reduction to the red salt takes place at once, or whether the solution actually contains cupric sulphite, which is reduced only on standing or heating.

Moist cupric hydroxide, previously washed until free from sulphate, was placed in a beaker surrounded by ice-water, and sulphur dioxide passed in until the solution was complete. The blue hydroxide is first converted into a yellowish substance; this gradually dissolves to a dark-green solution. In the cold this solution may be preserved for a considerable time without change, but on standing for a few hours, or immediately on warming, it throws down a heavy crystalline deposit of the red salt, while the solution becomes nearly colorless.

In order to determine whether the reduction to the red salt had already taken place in the green solution, the amount of sulphuric acid present in a given volume was determined, while an equal volume was heated to boiling, and the sulphuric acid contained in it was determined after the separation of the red salt. In the first case this could not be done by acidification and precipitation with barium chloride, since by this process cupric chloride is formed, and is immediately reduced by the sulphur dioxide present with formation of sulphuric acid. The green solution was therefore carefully precipitated by barium hydroxide, and the resulting mixed precipitate of sulphite and sulphate exhausted on the filter with hot hydrochloric acid.[1] One experiment gave the following result:

Before boiling, the green solution gave 0.0520 $BaSO_4$.

After boiling, an equal volume gave 0.3404 $BaSO_4$.

In this case a very slight separation of the red salt had already taken place before the determination. With care, keeping the material quite cold, it is possible to obtain a solution of cupric hydroxide in sulphurous acid, which is free from sulphuric acid. These experiments show that no reduction to cuprous compounds takes place in dissolving cupric hydroxide in sulphur dioxide solution, and that in the green solution all the copper present is in the cupric condition.

All attempts to obtain a crystalline cupric sulphite by evaporation of the solution were without result, as in every case a deposit of the red salt was soon formed.

It was noticed that, on exposure to the air, the green sulphurous-acid solution of cupric hydroxide becomes covered with a yellow film. On passing a current of air through the liquid, the solution first becomes nearly black, then gradually throws down a precipitate of a bright yellow-ochre color. The same substance is obtained as a flocculent yellow precipitate on addition of alcohol to the solution. This compound dries in the air to a bright-yellow powder. It dissolves in dilute hydrochloric acid to a green solution, giving off sulphur dioxide, and without separation of cuprous chloride, and in dilute sulphuric acid without separation of metallic copper; this behavior shows it to be a cupric compound. From its character and mode of formation it appeared probable that the compound is a basic cupric sulphite. This view was fully confirmed by a study of the composition and reactions of the substance.

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[1] This could also have been done by boiling the solution with sodium carbonate, and after filtering off the copper oxide separated, determining the sulphate in the solution of sodium salts.

Basic cupric sulphite.—This compound was prepared in considerable quantities in the following manner: Cupric hydroxide was precipitated in the presence of ammonium sulphate, and washed repeatedly by decantation through a cotton-cloth filter until free from sulphate. The cupric hydroxide was brought upon a cotton filter and freed from most of the water by suction; the stiff paste was placed in a beaker surrounded by water at 0°, and a rapid current of washed sulphur dioxide passed in until complete solution resulted. The green liquid was then poured into twice its volume of 90-per cent. alcohol, and the precipitate collected by suction on a filter. The wet precipitate was then repeatedly washed by agitating with water, and filtration, until the filtrate no longer showed the presence of soluble sulphates. The material is slightly soluble in water, communicating a green tint to the washings. This color disappears at once on the addition of a few drops of hydrochloric acid, showing that the sulphite has a much greater coloring power than the chloride. The precipitate was finally washed twice with alcohol, and allowed to dry spontaneously in the air. So prepared, it is an amorphous powder of bright yellow-ochre color. Dried at 100° in air, hydrogen or carbon dioxide, it loses some sulphur dioxide, and changes in color to grayish-brown. The substance was therefore analysed in the air-dry condition, and the results calculated for material dry at 100°. For this purpose it was necessary to determine the moisture present in the air-dry samples. This was accomplished by heating to 100°–110°, in a current of dry hydrogen or carbon dioxide; the sulphur dioxide given off on drying was estimated by passing the gas through bromine water, and subsequently determining the sulphuric acid formed, by means of barium chloride. The amount of sulphur dioxide given off on drying proved to be slight, but was sufficient to make it impossible to obtain absolutely constant weight. The determinations of copper were made by the battery in sulphuric-acid solution; those of sulphur by oxidation by boiling with bromine water and precipitation of the sulphur as barium sulphate. The substance being a copper compound, the method of titrating the sulphur dioxide by standard iodine solution could not be employed. The determination of water of constitution presented great difficulties, owing to the fact that it is given off together with much sulphur dioxide at about 160°. Owing to the liberation of sulphur dioxide, the estimation of the water by direct weight gave rather variable results. The determinations were finally made by gently igniting the substance in a combustion-tube in a current of dry carbon dioxide, conducting the gas from the tube into bromine water and subsequently estimating the sulphuric acid formed in the latter. The loss of weight of the substance, *minus* the weight of the sulphur dioxide, was taken as the amount of combined water. These determinations are, however, not wholly satisfactory, as the material gradually loses some water and sulphur dioxide at all temperatures between 100° and 160°, and it is impossible to draw the line sharply between hygroscopic and combined water. At about 160°, however, the substance suddenly undergoes complete decomposition, contracting much in volume, and becoming reddish-brown in color.

A number of samples, separately prepared, were analysed, with results which show that the substance, though unstable, is of perfectly definite composition, and has the formula $3CuO.2SO_2$, with probably 1½ molecules of water.

	Calculated for $3CuO.2SO_2.1\frac{1}{2}H_2O$.	Found.				
		I.	II.		III.	IV.
Cu	48.38	48.68	48.46	48.39	48.60	48.65
S	16.28	15.87	15.86	15.83	16.39	16.23
O	28.48	...	...	...	...	...
H_2O	6.86	...	6.19	...	6.98	6.64

On boiling with water, the compound undergoes a complete decomposition, which strongly supports the above view of its constitution. On boiling for a few minutes, it gives a deep-blue solution of copper sulphate, and a brown insoluble substance, which is completely converted by hydrochloric acid into cuprous chloride with liberation of sulphur dioxide, and dissolves in sulphuric acid with separation of metallic copper. This substance thus appears to be cuprous sulphite, formed according to the reaction

$$3CuO.2SO_2 = CuSO_4 + Cu_2SO_3.$$

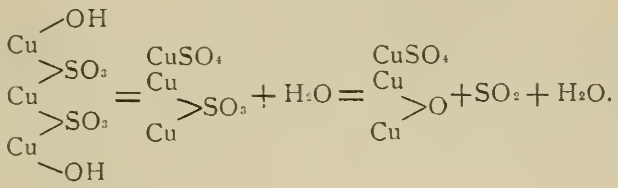
On continuing the boiling with water, sulphur dioxide is given off, and finally bright-red cuprous oxide remains, suspended in blue solution of cupric sulphate:

$$3CuO.2SO_2 = CuSO_4 + Cu_2O + SO_2.$$

If this equation be correct, one-third of the copper should appear as cupric sulphate, and two-thirds as cuprous oxide. A quantitative experiment gave the following results: 0.5000 gram of air-dry substance (containing 13.18 per cent. moisture, and corresponding to 0.4341 gram dry substance) gave—

	Calculated.		Found.	
	In $CuSO_4$.	In Cu_2O.	In $CuSO_4$.	In Cu_2O.
Cu	0.0700	0.1400	0.0717	0.1407

If it is assumed that a portion of the water present exists in the form of cupric hydroxide, the above reactions may, perhaps, be correctly represented by the following graphic formulas:



$$\begin{array}{l} Cu{-}OH \\ \quad >SO_3 \\ Cu \\ \quad >SO_3 \\ Cu{-}OH \end{array} = \begin{array}{l} CuSO_4 \\ Cu \\ \quad >SO_3 \\ Cu \end{array} + H_2O = \begin{array}{l} CuSO_4 \\ Cu \\ \quad >O \\ Cu \end{array} + SO_2 + H_2O.$$

The same transformation takes place also on heating the dry substance to 160°, since the residue, on treating with water, gives at once a blue solution of cupric sulphate.

The ready conversion of basic cupric sulphite into the red cuproso-cupric sulphite indicates that the two compounds are similarly constituted. Further experimental work is, however, necessary, in order to determine the precise relation between them. It appears probable that further study of the basic cupric sulphite, and of the cuproso-cupric sulphite and cuprous sulphite, into which it is so easily transformed, will, on account of the simple decompositions which these compounds undergo, throw important light on the structure of the sulphites.

When moist basic cupric sulphite is exposed to the air it is gradually oxidised, forming cupric sulphate, which may be dissolved out in water, leaving a yellowish-green insoluble powder which gives all the reactions of the original substance. It is probably a basic cupric sulphite of simpler constitution than the one described above, but further study is necessary to determine its exact nature.

In conclusion, attention may be called to the interesting relation which exists between the sulphites and carbonates of copper. As with sulphurous acid, copper forms with carbonic acid no neutral salts, the only cupric carbonates known being azurite, $3CuO.2CO_2.H_2O$, and malachite, $2CuO.CO_2.H_2O$. It will be seen that the basic cupric sulphite, $3CuO.2SO_2.1\frac{1}{2}H_2O$, described in this paper, corresponds closely in its constitution with azurite. Cupric oxide is a weak base, and with weak acids, such as carbonic or sulphurous acids, it appears to be incapable of entering into combination in the proportion necessary to form neutral salts. The basic carbonates, like the basic sulphite, are decomposed on boiling with water, the carbonates giving off carbon dioxide and leaving cupric oxide. The difference in the two reactions

$$3CuO.2SO_2 = CuSO_4 + Cu_2O + SO_2$$
$$3CuO.2CO_2 = 3CuO + 2CO_2$$

is doubtless due to the capacity of sulphur to form a higher acid-forming oxide than SO_2, a power not possessed by carbon, and also, perhaps, to a fundamental difference in the structure of the sulphites and carbonates.

REVIEWS AND REPORTS.

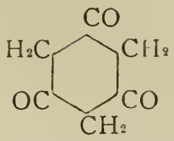
Tautomerism.

It has been known for some time that two different chemical substances could be represented correctly by the same structural formula. This peculiar kind of isomerism Wislicenus calls geometrical isomerism, and under the name of stereochemistry[1] there has been developed a theory to explain it by an extension of the Van't Hoff and Le Bel hypothesis of the space relation between the atoms or groups of atoms.

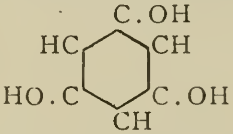
The opposite conception, that the constitution of the same chemical compound under different circumstances could be accurately represented by two totally different structural formulas, has now become quite general. Compounds which belong to this class seem to possess a double character, appearing in one reaction to have one constitution and in another to have an entirely different structure. Thus Von Baeyer[2] found that phloroglucin gave a trioxime with hydroxylamine, and was undoubtedly to be regarded as a ketone derived from hexamethylene, *i. e.* a 1, 3, 5 keto-hexamethylene:

[1] This Journal **9**, 453.

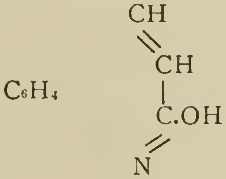
[2] Ber. d. chem. Ges. **19**, 159.



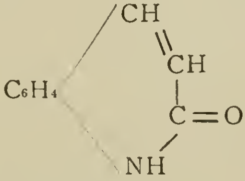
Its reactions in general, however, showed it to be plainly a trihydroxy-benzene having the following formula:



Other substances have been shown to exhibit a like conduct. Carbostyril, for example, yields, according to Friedländer,[1] two alkyl carbostyrils, $C_9H_6(OR)N$ and $C_9H_6O(NR)$, when treated with an alkali and an alkyl halogen. This would seem to indicate that carbostyril existed, or at least reacted, in two forms, the first having the formula



i. e. a lactim; and the second a lactam formula,



To explain this peculiar chemical conduct, Baeyer assumes the existence of pseudo or unstable forms. These pseudo forms are conceived as resulting from a change of position of the hydrogen atoms within the molecule, and may be determined by certain reactions. Thus phloroglucin is undoubtedly a trioxybenzene, and yet the reaction with hydroxylamine shows that it exists also in the form of a ketone. Hence 1, 3, 5 trioxybenzene is called phloroglucin, and the 1, 3, 5 keto-hexamethylene, pseudo-phloroglucin by Baeyer.

In 1885 C. Laar[2] published an article entitled "Ueber die Möglichkeit mehrerer Strukturformeln für dieselbe chemische

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[1] Ber. d. chem. Ges. **18,** 1528; **20,** 2009.

[2] Ibid. **18,** 648; see also **19,** 730.

Verbindung," in which he enumerates the most important compounds showing this peculiar conduct. To this phenomenon he gives the name of tautomerism (ταὐτό, the same, and μέρος, parts). Compounds like phloroglucin, carbostyril, etc., are called tautomeric. To explain tautomerism, Laar assumes that, according to the principle of changing combination within the molecule of a tautomeric body, a constant change of place of the easily mobile hydrogen atom occurs, so that the different arrangements of the hydrogen atoms corresponding to the structural formulas deduced are to be regarded merely as phases of an intramolecular motion. Thus to take the simplest case mentioned by him, viz. hydrocyanic acid. The chemical conduct of this substance may be represented by the two tautomeric formulas,

$$H - C \equiv N \text{ and } H - N = C.$$

In the first of these formulas the hydrogen atom is represented as connected with the carbon atom; in the second with the nitrogen atom, and Laar conceives of the hydrogen atom as oscillating alternately between the one and the other position. Both forms must exist in solution together, therefore, according to Laar.

Most chemists, however, are inclined to agree with Baeyer[1] that the phenomenon designated by Laar as tautomerism is rather to be explained by assuming the existence of unstable atom groupings (pseudo forms) besides the stable groupings, *i. e.* the normal positions of equilibrium, and that therefore each of the molecular arrangements designated by Laar as tautomeric really possesses a definite constitution.

For the expression tautomerism made use of by Laar, the more exact designation desmotropism (δεσμός, bond, and τροπή, changing) has been suggested by P. Jacobson,[2] according to Victor Meyer. Hantzsch and Hermann[3] employ both these expressions, but they use each in a different sense. The characteristic property shown by certain compounds of reacting in different ways in typical reactions is to be designated according to them as tautomerism, while a body exhibiting such conduct could be called briefly tautomeric. Now this property of tautomerism depends upon the easy mobility of the hydrogen atoms within the molecule. As a designation, therefore, of the actual change of union taking place and the new distribution of the hydrogen atoms within the molecule of a tautomeric body thereby conditioned, the expression desmotropism alone is used. The arrangement of the atoms within this molecule, determined by the different conduct of a tautomeric compound, and distinguished by a different distribution of hydrogen atoms, may be called the desmotropic condition.

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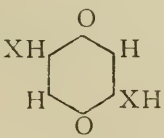
[1] Ber. d. chem. Ges. **16**, 2188.

[2] Ibid. **20**, 1732, foot-note.

[3] Ibid. **20**, 2801.

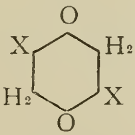
The structural formulas corresponding to the different desmotropic conditions bear the same relation to each other that the formulas of isomeric bodies do, but Hantzsch and Hermann hold that the characteristic distinction of desmotropism as opposed to isomerism is that under definite physical conditions only a single one of the desmotropic forms is stable, at least in the solid state. However, a tautomeric body under changed external conditions may assume another desmotropic form. This change will become known by the appearance of the body in question in another form having different physical properties. Thus succino-succinic ether and a number of its derivatives, according to Hantzsch and Hermann, are shown by their chemical conduct to be tautomeric. These react sometimes as quinones, sometimes as hydroquinones, *i. e.* in the sense of the desmotropic conditions distinguished by the atom grouping $—CO.CH(COOC_2H_5)$ and $—C(OH)C(COOC_2H_5)$. Now Lehmann[1] has shown that many of these tautomeric derivatives of succino-succinic ether also exhibit di- and trimorphism, and that these different crystal forms may be readily changed one into the other by changing the external conditions. Hantzsch and Hermann endeavor to connect these different crystal forms with the different desmotropic conditions. Thus they say for the atom system $C_6O_2H_4(COOC_2H_5)_2$ there are three possible desmotropic conditions and three physically different forms. They assume that those forms having color belong to the group of quinones, since Graebe and Liebermann have shown that bodies belonging to the group of the quinones have color; and thus they deduce the following formulas:

I.



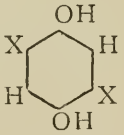
Stable, rhombic, colored.

II.



Unstable, asymmetric, colored.

III.



Unstable, asymmetric, colorless

Quinone dihydro para-dicarbonic acid ether.

Hydroquinone dicarbonic acid ether.

$$X = (COOC_2H_5).$$

Nef[2] asserts that this question of color is purely arbitrary and proves nothing whatever regarding the structural formula of the substance, and then he shows that the third modification of ethyl p-dihydroxy-terephthalate to which Hantzsch and Hermann give the hydroquinone formula (III.) is *not* colorless, but has quite a marked color. He states that the only chemical evidence brought forward by Hantzsch and Hermann in favor of the tautomerism of hydroquinone compounds is the fact that ethyl tetraoxyterephthalate and ethyl quinone-dioxyterephthalate form dioximes with hydroxylamine. From the method of formation of these substances and careful analyses Nef shows them to be oxyammonium salts and *not* oximes. "There is, therefore," he continues, "absolutely no reason for assuming the existence of tautomerism or desmotropic conditions in the succino-succinic acid series. The polymorphism in this group is probably due to physical isomerism, just as has been so conclusively shown by Larsen[1] to be the case with the hydroxamic acids." Nef regards ethyl succino-succinate as nothing but dihydro-dioxyterephthalic ether (formula III.), and explains the reaction with phenylhydrazine as forming not a hydrazone, as would be the case with a ketone, but as forming a hydrazide in accordance with the equation:

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[1] Zeit. für Krystallog. **10**, 344.

[2] This Journal **11**, 1; **12**, 379.

$$C_6X_4 < \begin{matrix} OH + HHN-NHC_6H_5 \\ OH + HHN-NHC_6H_5 \end{matrix} = C_6X_4 < \underset{\text{Hydrazide.}}{\begin{matrix} NH-NHC_6H_5 \\ NH-NHC_6H_5 \end{matrix}} + 2H_2O.$$

The reaction of phloroglucin with phenylhydrazine, as shown by Von Baeyer,[2] is in favor of this view, a hydrazide being formed here also.

Nef doubts the existence of tautomeric or pseudo-forms altogether, and says that, "In order to explain the behavior of such tautomeric substances the assumption has to be made that, according to the reagent acting on them, the hydrogen is bound either to carbon or to oxygen. Such an explanation has unquestionably much against it, and, especially since it attacks the foundation of modern structural chemistry, it is of the utmost importance that the most convincing proofs be brought forward to justify it."

In a later article Nef[3] takes up the question of the constitution of aceto-acetic ether. He concludes from its chemical conduct that the sodium compound of aceto-acetic ether must have the following formula:

$$CH_3-CONa=CH-CO_2R,$$

the sodium being joined to carbon by means of oxygen. To the free aceto-acetic ether Nef gives the hydroxyl formula:

$$CH_3-COH=CH.CO_2R,$$

regarding it as β-oxycrotonic acid ether. The reaction with phenylhydrazine or with hydroxylamine is, according to him, no longer sufficient to establish the ketone nature of aceto-acetic ether, since it has been shown that phenols react with amines, with phenylhydrazine or with hydroxylamine as readily as aldehydes or ketones do. Assuming the hydroxyl formula for aceto-acetic ether, the first product of the action of phenylhydrazine must be a hydrazide having the following formula:

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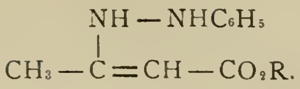
[1] Ann. Chem. (Liebig) **252**, 170.

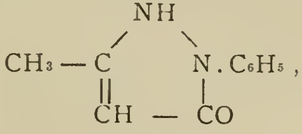
[2] Ber. d. chem. Ges. **22**, 2189.

[3] Ann. Chem. (Liebig) **266**, 52.



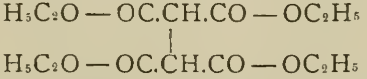
$$\begin{array}{l} \quad\;\; NH - NHC_6H_5 \\ \quad\;\; | \\ CH_3 - C = CH - CO_2R. \end{array}$$

This would then yield a pyrazolon derivative,



in which there is an imido group which should have acid properties. If, on the other hand, the ketone formula be the correct one, then a hydrazone must be the first product of the reaction between aceto-acetic ether and phenylhydrazine, and it is difficult to see how this could yield a pyrazolon derivative with an acid imido group.

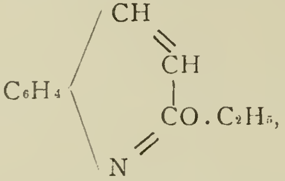
Nef has not only succeeded in isolating the hydrazide in solid condition and in showing that like hydrazobenzene it yields an azo-derivative (phenyl-β-azocrotonic acid ether) on oxidation with mercuric oxide, but he has also shown that the pyrazolon derivative, made from the hydrazide, has strong acid properties, owing to the presence of the imido group. The fact that aceto-acetic ether or the methyl or ethyl derivative can be perfectly smoothly converted into their sodium salts without any reduction of the aceto-acetic ether taking place, shows plainly, according to Nef, that these substances are not ketones. Further, he states that a methylene group (CH_2) between two carbonyl groups does *not* possess acid properties, as it would be necessary to assume if the ketone formula be accepted for aceto-acetic ether, and he cites in proof of this statement the cases of malonic acid ether, $C_2H_5O - CO - CH_2 - CO - OC_2H_5$, as well as the ether of acetylene tetracarbonic acid,



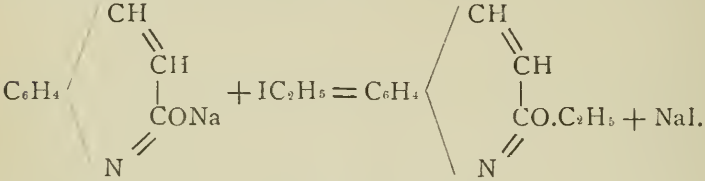
$$\begin{array}{l} H_5C_2O - OC.CH.CO - OC_2H_5 \\ \qquad\qquad\quad\;\; | \\ H_5C_2O - OC.CH.CO - OC_2H_5 \end{array}$$

. Neither of these substances has acid properties. "It is accordingly," continues Nef, "highly probable that the free aceto-acetic ether is β-oxycrotonic acid ether, $CH_3 - C(OH) = CH - CO_2R$, and the mono substituted aceto-acetic ethers are alkyl derivatives of β-oxycrotonic acid ether, $CH_3 - C(OH) = CR - CO_2R$. These bodies show no tautomerism or desmotropism, and the assumption of a pseudo-ketone formula, according to our present knowledge, is just as little correct here as in the case of the succino-succinic ether; for the hydroxyl formula is sufficient to explain all the reactions of this body, especially all the condensations which have been brought about with it."

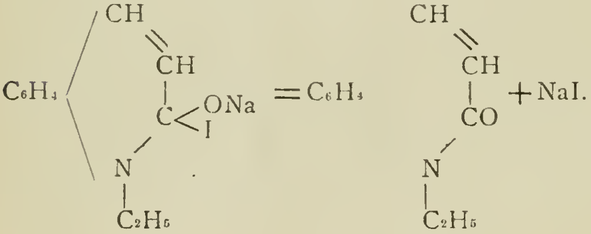
Having thus shown that tautomerism probably does *not* exist in the case of aceto-acetic ether and derivatives, as well as with the succino-succinic ether and derivatives, Nef next takes up the case of carbostyril. Friedländer and Weinberg[1] have shown that the silver salt of carbostyril, when treated with ethyl iodide, gives exclusively an oxygen ether,



while the sodium salt of carbostyril treated in the same way yields a mixture of equal parts of the oxygen and nitrogen ethers, according to the equations:



Oxygen ether.



Nitrogen ether.

The direct replacement of the sodium by the ethyl group when the sodium salt of carbostyril is treated with ethyl iodide appears to be much more difficult, on account of the strongly positive nature of the sodium. An addition of the elements of ethyl iodide takes place, therefore, at the same time that the sodium is replaced, and there results a mixture of the two ethers. Knorr[2] has found that γ-methyl-carbostyril sodium also yields a mixture of the oxygen and nitrogen ethers when treated in the same way. Isatin shows the same conduct. Baeyer and Oekonomides have shown that the silver salt of isatin reacts with alkyl iodides to form exclusively the oxygen ethers. The sodium salt, however, according to Comstock and Kleeberg, yields only (?) the nitrogen ether, an addition of the constituents of ethyl iodide first taking place, thus

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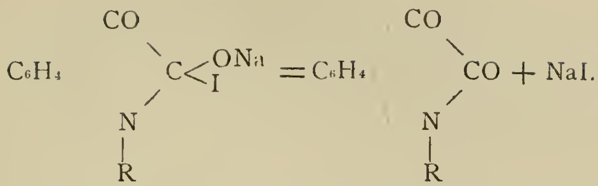
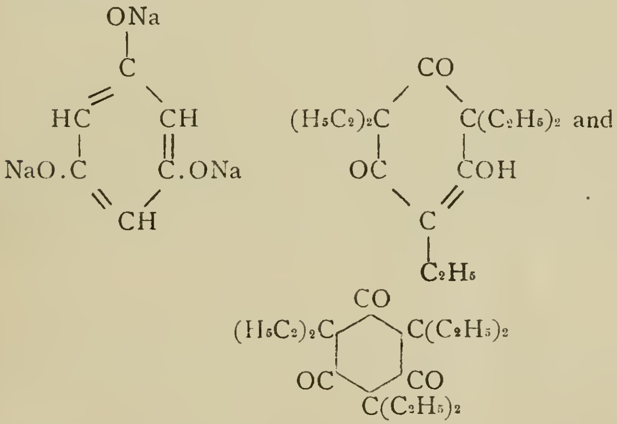
[1] Ann. Chem. (Liebig) **238**, 175.

[2] Ibid. **236**, 87.



The assumption that the silver salt is differently constituted from the sodium salt is very improbable, since in many cases from both salts the same ether results.

The same explanation holds for cases of desmotropism among the phenols reported by Herzig and Zeisel. Thus the sodium salt of phloroglucin is converted by ethyl iodide into penta-ethyl and hexa-ethyl phloroglucin, an addition product being first formed.



The formation of these compounds makes it exceedingly probable that there are three cases of double union in the benzene molecule.

While silver cyanide, $Ag-N=C$, generally forms with alkyl iodides isonitriles, $R-N=C$, a direct replacement of the metal taking place, potassium cyanide, $K-N=C$, forms as a rule alkyl cyanides when treated in the same way, an addition product, $K-N=\underset{\displaystyle I}{\underset{|}{C}}-R$, being first formed and then the organic cyanide, by the splitting off of potassium iodide. It should be noted that isonitriles sometimes result from potassium cyanide, $K-N=C$, as for example when the cyanide is treated with salts of the alkyl sulphonic acids. In this case, as in the case of the silver cyanide, $Ag-N=C$, a direct replacement of the metal probably takes place.

Nef concludes his article by saying: "It appears, therefore, to me that the conception of tautomerism and desmotropism, as well as the conception of unstable or pseudo-forms which have become so general in organic chemistry, are by no means justified, and owe their origin to inexact knowledge of the reactions which take place in such cases." W. R. ORNDORFF.

OUTLINES OF THEORETICAL CHEMISTRY. By LOTHAR MEYER. Translated by P. Phillips Bedson and W. Carleton Williams. With a preface by the author. London: Longmans, Green & Co., 1892.

A notice of the original book of which we now have this English translation appeared in the last volume of this journal (Vol. 13, p. 429). The translators have already rendered English-speaking chemists a good service in preparing their edition of Lothar Meyer's "Die modernen Theorien der Chemie," and it appears from an examination of this new volume that they have shown the same care in its preparation as in that of the larger book. Further, as we are told, "the revised sheets have been submitted to the author."

The object of the book is expressed by the author in his preface as follows: "In writing this work I have not considered the requirements of students alone, but have been desirous of offering something to those friends of scientific investigation who have neither the intention nor the time to concern themselves with the details of chemical investigation, but wish to become acquainted with the general conclusions arrived at." I. R.

A DICTIONARY OF CHEMISTRY. By T. E. THORPE, B. Sc. (Vict.), Ph. D., F. R. S., assisted by eminent contributors. In three volumes. Vol. 2. London and New York: Longmans, Green & Co., 1891.

The first volume of this extremely valuable work appeared in 1890 and it was noticed in Volume 12, p. 280. All who have had occasion to use the first volume will welcome the second, which is "like unto it" in everything that one seeking information on subjects in the field of applied chemistry can ask for. It begins with Eau de Cologne and ends with Nux Vomica. Among the longer and more important articles included in it are the following: Fuel, by B. H. Brough; India-rubber, by C. A. Burghardt; Glycerin, by W. Lant Carpenter; Matches, by E. G. Clayton; Explosives, by W. H. Deering; Fermentation, by Percy F. Frankland; Indigo, Lakes, Litmus, Madder, by J. J. Hummel; Furfurol, Hydrazone coloring matters, by Francis R. Japp; Leather, by H. R. Proctor; Glass, by W. Ramsay; Emery, Fire-clay, Granite, Jade, etc., by F. W. Rudler; Gum-resins, Mucilage, Musk, by Alfred Senier; Iodine, by E. C. C. Stanford; Iron, by Thomas Turner; Artificial manure, Nitrification, by R. Warington; Indamines and Indophenols, by Otto N. Witt; Coal Gas, by Lewis Wright.

The closing paragraph of the notice of the first volume applies with equal force to the second: "The chemist, whether engaged in technical work or not, will find the book of great value, and he will hardly look for information without finding it. There is, in fact, no other book in English or in any other language that gives as fresh and as reliable information on subjects connected with industrial chemistry." I. R.

HÜLFSBUCH ZUR AUSFÜHRUNG CHEMISCHER ARBEITEN FÜR CHEMIKER, PHARMACEUTEN UND MEDICINER. Von Dr. HUGO SCHWANERT, ordentlichem Professor der Chemie an der Universität Greifswald. Dritte umgearbeitete Auflage. Braunschweig: C. A. Schwetschke und Sohn. 1891.

This book has long been known and has proved of value to many in the laboratory. In the new edition it is brought down to date. It has to deal with the methods in use in analytical laboratories, the subject-matter being taken up under the following heads: I. Analytic investigations of inorganic substances; II. Analytic investigations of organic substances; III. Systematic course of an analytic investigation; IV. Separation of the elements of the different groups; V. Preparation and testing of chemical preparations; VI. Gravimetric investigations; VII. Volumetric investigations; VIII. Investigation of water and articles of food; IX. Detection of poisons and blood; X. Zoöchemical investigations.

As will be seen, the book covers more ground than is usually covered by treatises on analytical chemistry, and yet everything is included within 394 pages. Obviously no single subject can be treated very fully. In a great many cases, however, "just what is wanted" will be found. I. R.

LABORATORY PRACTICE, A SERIES OF EXPERIMENTS ON THE FUNDAMENTAL PRINCIPLES OF CHEMISTRY, A COMPANION VOLUME TO THE NEW CHEMISTRY. By JOSIAH PARSONS COOKE, LL. D. New York: D. Appleton & Co., 1891.

Anything written by Professor Cooke on the subject of chemistry must be of interest to chemists, and especially is this true of anything touching the methods of teaching the elements of chemistry, an extremely difficult subject, and one to which Professor Cooke has given much attention. The book before us contains directions for a number of comparatively simple experiments in chemistry and physics. It differs markedly from many books having the same object, in that it does not attempt to "teach all the principal facts of the science in six weeks." The number of experiments described is small, but the work required in each case involves the expenditure of some time, so that each experiment is thus more likely to make a lasting impression. The very important truth is recognised that it is better to teach a few things well than many superficially. In the introduction the author says: "This book is not intended to be used without a teacher." . . . "The educational value of such a course as is here outlined depends entirely on the manner in which the work is directed and supervised. The student should be instructed, by continued reiteration, if necessary—

1. To observe the minutest particular in regard to every experiment.
2. To distinguish essential from non-essential phenomena.
3. To draw correct inferences from the results.
4. To express concisely but clearly in writing the facts observed and conclusions reached."

The more frequently these words of caution are brought to the attention of teachers the sooner shall we reach the stage when laboratory courses will have educational value. It is certainly true that at present many sins are committed under the name of "teaching elementary science." I. R.

METHODS OF GAS ANALYSIS. By Dr. WALTHER HEMPEL, Professor of Chemistry in the Dresden Polytechnicum. Translated from the second German edition by L. M. DENNIS, Assistant Professor of Analytical Chemistry in Cornell University. 8vo. Macmillan & Co., London and New York, 1892.

The subject of gas analysis has become, at the present time, so important, both from a scientific and a technical point of view, that the appearance of an English translation of this book by so competent an authority and investigator as Professor Hempel will be welcomed by all English-speaking chemists. The translation is practically a revision of the second German edition under the direction of the author and by one of his pupils. Several of the illustrations have been changed and improved, all the data have been revised and brought up to date, new methods which have been tried and found to work satisfactorily have been introduced, and the English edition is really better than the present German one. All references are given, and care seems to have been taken to verify these as well as all the equations made use of. Some of the formulas of the German edition have been corrected, and tables giving the atomic weights, the reduction of a gas volume to 0° and 760 mm., the tension of aqueous vapor, and the theoretical densities and the weights of one liter of the gases, all of which will be of great use to the student, have been added to the English edition. A full and complete index which includes all authorities cited is another point in which the English translation is superior to the German edition.

The book is singularly free from all kinds of errors, is well printed and bound, and is of convenient size and shape for a text-book and laboratory manual. The illustrations, of which there are quite a number, are neat and well drawn, the type clear and of a size easy to read.

The translation is in clear and forcible English and true to the original. The contents are divided into three parts. Part one has to do with the general methods of gas analysis, including the collection and keeping of gases, and a description of the apparatus, laboratory, and appliances used in both technical and exact gas analysis. Part two is taken up with the special methods of gas analysis, and part three with the practical applications of gas analysis to the analysis of furnace gases, illuminating gas, etc., etc. Altogether the work is an admirable exposition of the subject and one that no analytical chemist can afford to be without.

W. R. O.

A TEXT-BOOK OF ELEMENTARY CHEMISTRY, THEORETICAL AND INORGANIC. By GEORGE F. BARKER, M. D. Second edition, revised and enlarged. Louisville, Ky. : John P. Morton & Co., 1891.

The first edition of this book appeared at a time when the chemists of this country were learning to accustom themselves to what is generally somewhat vaguely called "Modern Chemistry," the chemistry which is founded upon Avogadro's law, the new atomic weights and our present conceptions of valency and constitution, and Professor Barker did the country a service in bringing the new ideas in elementary form before chemists. His book has been used extensively and has been helpful to many. In regard to the second edition now before us the author says : "The gratifying success achieved by the first edition of this book seems to make it undesirable, in revising it, to alter materially its general plan. In this edition, therefore, the framework has been allowed to remain in much the same form as that in which it was originally constructed." The periodic law is made the guide in the classification of the elements, and in general the treatment is up to the times.

I. R.

LEHRBUCH DER TECHNISCHEN CHEMIE. Von Dr. H. OST, Professor der Technischen Chemie an der Technischen Hochschule zu Hannover. Berlin : R. Oppenheim, 1890.

Prof. Ost's book is a volume of 700 pages with 200 woodcuts : the type and illustrations are excellent. It is a concise, clearly written text-book for students of technical chemistry. It includes descriptions of the latest improvements and discoveries in this branch, and can be cordially recommended as a book for study.

E. R.

HANDBUCH DER PHOTOGRAPHIE. Von PROF. DR. H. W. VOGEL, Vorsteher des photochemischen Laboratoriums, der Königlichen technischen Hochschule Berlin-Charlottenburg, Herausgeber der Photographischen Mittheilungen. Vier Theile, enthaltend Die photographische Chemie, Optik, Praxis und Aesthetik. I. Theil. Photochemie und Beschreibung der photographischen Chemicalien. Vierte, gänzlich umgearbeitete, verbesserte, und vermehrte Auflage. Verlag von Robert Oppenheim: Berlin, 1890. 351 Seiten. 8vo.

This belated notice has too long been due Professor Vogel's book. No one is better qualified than the author to treat of anything in the realm of photography, an art which he has done so much to advance to its present high condition. All who are interested in the chemical side of photography should have this book available for reference. It is written with true German thoroughness, and the subject is dealt with in the true scientific spirit. It goes without saying that the matter is brought up to date in this new edition. Water taken direct from the spring is pretty sure to be fresh. I. R.

MANUAL OF CHEMICAL TECHNOLOGY. By RUDOLF VON WAGNER. Translated and edited by WILLIAM CROOKES, F. R. S., from the thirteenth enlarged German edition as remodeled by Dr. Ferdinand Fischer. With 596 illustrations. D. Appleton & Co., New York, 1892. 968 pp.

This is a large volume of 950 closely printed pages with about 600 woodcuts. This useful book of reference covers the whole field of applied chemistry. Fuel, lighting, metallurgy, the manufactures of inorganic and organic chemical products, glass and earthenware, articles of food, and the technology of fibres, including dyeing and tissue-printing, are treated briefly but clearly. The chapters on fuel, on the metallurgy of iron, silver, and gold, are very good.

A section by the editor on the qualitative examination of coloring matters completes the excellent chapter on the benzene dyestuffs; that on dyeing and tissue-printing is equally good. On the whole the editor has brought the book well up to date; an exception is the article on aluminium, in which no mention is made of working electric processes for obtaining pure aluminium, though the Cowles process for making alloys is described. There are works at Neuhausen on the Rhine where aluminium is made by electricity, and in this country pure aluminium, made in quantity by the Hall process in Pittsburgh, has been on the market for three years at prices much lower than those asked for aluminium formerly.

The woodcuts are printed from well-worn German blocks, lettered in sometimes nearly illegible German script, necessitating a translation of the German words with the cuts. These are minor drawbacks. The work is of great value to all interested in chemistry, metallurgy or manufactures. E. R.

GRUNDLAGEN DER CHEMIE. Von D. MENDELEJEFF, Professor an der Universität in St. Petersburg. Aus dem Russischen übersetzt von L. Jawein, Docent am Technologischen Institut in St. Petersburg, und A. Thillot, Assistant am chemischen Laboratorium des Technologischen Instituts in St. Petersburg. Carl Ricker: St. Petersburg, 1891. (Lieferungen 2–8.) 1126 pp. 8vo.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEFF. Translated from the Russian (Fifth edition) by George Kamensky, A. R. S. M., of the Imperial Mint, St. Petersburg; edited by A. J. Greenway, F. I. C., sub-editor of the Journal of the Chemical Society. In two volumes. Longmans, Green & Co., London and New York, 1891.

When the first number of the German translation of Mendeléeff's work appeared, about two years ago, attention was called to it in this Journal in appreciative terms. Now the work is complete, and it is clear that it abundantly fulfills the promise of the first number. As was said in the earlier notice: "Every teacher and every advanced student of chemistry should read and study this book with care. Even the most experienced will find much in it that will prove of value to him."

All the world knows that Prof. Mendeléeff has marked originality, and it is not surprising that his book is not cast in an ordinary mould. Everything that one could expect to find in a book of this size is probably to be found here, but it is, of course, in the method of treatment that the originality appears. The treatment is above all things philosophical. The writer is not satisfied with giving an account of the occurrence, preparation, and properties of a lot of substances, with a few crude suggestions in regard to their constitution. Each thing, each phenomenon suggests to him something else. If the particular thought that comes to him cannot be fitted into the text proper, a foot-note appears. Foot-notes abound as in no other book on chemistry. They form probably half the contents. But they are for the most part of special interest.

In the preface to the fifth Russian edition the author uses these words: "Experimental and practical data occupy their place, but the philosophical principles of our science form the chief theme of the work. In former times sciences, like bridges, could only be built up by supporting them on a few deep abutments and long girders. In addition to the exposition of the principles of chemistry, it has been my desire to show how science has now been built up like a suspension bridge, supported by the united strength of a number of slender but firmly fixed threads, which individually are of little strength, and has thus been carried over difficulties which before appeared impassable. In comparing the science of the past, the present, and the future, in placing the particulars of its restricted experiments side by side with its aspirations for unbounded and infinite truth, and in restraining myself from yielding to a bias towards following the most attractive representation, I have endeavored to incite in the reader a spirit of inquiry which, unsatisfied with speculative reasonings alone, should subject every idea to experiment, excite the habit of stubborn work, necessitate a knowledge of the past, and a search for fresh threads to complete the bridge over the bottomless unknown. Experience proves that it is possible by this means to avoid two equally pernicious extremes, the Utopian—a visionary contemplation which proceeds from a current of thought only—and the realistic stagnation which is content with bare facts."

Those who have made up their minds on such matters as valency and constitution will be disappointed to find that Professor Mendeléeff does not accept the common ideas on these subjects, or rather his own ideas are much less rigid than these. But whether the reader agrees in all points with the author or not, he will be led to think by what he reads, and he will recognise in every page of the book an honest, earnest effort to discover the truth.

The English translation in two handsome volumes, one of 600, the other of 500 pages, has been prepared with the coöperation of the author. A fairly thorough examination shows that much more care has been taken in the rendering than is usual in the translation of works on chemistry into English. It is probable, considering the way in which the work has been done, that the English edition is quite as satisfactory as the German. Certain it is that both are extremely interesting reading, and it will be to the great benefit of chemistry if both are widely read and studied.

I. R.

NOTES.

Wolcott Gibbs Fund for Chemical Research.

On the 21st of February Dr. Wolcott Gibbs reached the age of 70 years, and a number of his friends united in showing their appreciation of his labors by collecting a fund to be known by his name, the income of which is to be devoted to the encouragement of chemical research. This fund, amounting to $2650, was put at the disposal of Dr. Gibbs, and an address presented to him on the morning of his birthday. The address, which was signed by one hundred and ten persons, is here given:

"The twenty-first of February, 1892, is not alone a day of importance to yourself and those nearest you, but it is also a day of rejoicing to us, who love you as a friend and comrade in the walks of life and science, and revere you as a teacher and leader in the love of truth.

It is rarely given to a man to look back from his seventieth birthday upon a lifetime devoted to the duties of patriotic citizenship and to the advancement of human knowledge, both by important discoveries and by imparting the spirit of scientific research to others. That this usefulness may continue undiminished for many years is the heartfelt wish with which we offer our congratulations.

Between the time when you first began your scientific career and to-day, a great change has come over Chemistry in America. Then there were not many institutions which could boast of a professorship in pure chemistry, and laboratory research was denied to all but a favored few; now laboratories exist throughout the country, in which earnest work is being accomplished—in not a few by men whose ardor was first kindled by you.

But, although we have the apparatus for research, the means to encourage it are still inadequate, and it is towards supplying this want that we must direct our hopes in the future. How appropriate is it, then, to mark, by a distinct step in this direction, the birthday of one whose efforts have played so conspicuous a part in what has already been achieved!

We therefore unite in establishing a fund for the encouragement of chemical research, to be known by your name, in memory of this day, and we request you to entrust it to such hands and couple it with such conditions as you may deem best. To this end we have gladly contributed our offerings, and, although the result is a measure of our several means rather than of our inclinations, we trust that you will accept it as a token of the affection and good wishes of your friends, associates and pupils."

To this address Dr. Gibbs replied as follows:

"*My dear Professors Jackson and Loeb,*—

May I beg you to present to those from whom I received, a few days since, so signal a mark of friendship and good-will, my heartiest, most earnest and most grateful acknowledgment? The address which I received on my seventieth birthday, signed by more than one hundred friends, pupils and assistants, brings back my youth in recalling the names of those who now join to offer me more than mere good wishes to cheer my advancing age. Their active friendship has taken the form which was most acceptable to me—that of an endowment to assist research in my own branch of science, so that I can feel that in a certain sense my power to work will not terminate with my life. As the generosity of my friends permits me also to dispose of the manner in which the endowment shall be administered, I submit to them through you the plan which seems to me best adapted to carry out their wishes—a plan which has been fully tested in somewhat similar cases, and found to work well in practice.

I therefore propose that the fund raised for endowment shall be given to the National Academy of Sciences, to hold the same in trust, and to invest and reinvest as may be necessary or advisable.

The income or interest of the fund shall be administered by a Board of Directors consisting of three persons, of whom at least two shall be members of the Academy. The first Board shall consist of Charles Loring Jackson, Thomas M. Drown and Ira Remsen, and the Directors shall have power to fill vacancies in their own number, notifying the Academy of their action without delay. In case of the deaths of all the members of the Board, their places shall be filled by persons holding professorships of chemistry, to be appointed by a vote of the Academy. The Directors shall make an annual report to the Academy, stating the condition of the fund and the appropriations made during the year. They shall have absolute and entire control of the disposition of the income of the fund, employing it in such manner as they may deem for the best interest of chemical science.

It is my belief that the above, or a similar arrangement, is the best which can be made—that is to say, the one which is most likely to be of permanent benefit to science. I trust that it will meet with the approbation of those who have honored me with their confidence and their regard.

Sincerely yours,

NEWPORT, March 1, 1892. WOLCOTT GIBBS."

At the meeting of the National Academy of Sciences held in Washington, April 19–22, the fund was accepted, and a resolution was adopted expressing high appreciation of the act of Dr. Gibbs in entrusting the fund to the Academy. I. R.

Stas.[1]

In the death of Prof. JEAN SERVAIS STAS, in Brussels, on the thirteenth of December, 1891, chemistry has lost one of its greatest and best known servants.

Born in Louvain in 1813, of poor parents, his student years were a prolonged struggle against difficulties. He, however, studied medicine and took the degree of M. D.; nevertheless, he felt that his bent was toward chemistry. When, before taking his degree, he had, in 1835, in conjunction with De Coninck, investigated the root-bark of the apple tree, he had been able to isolate a new crystalline substance, phloridzine, and to describe its properties. At this time there were only two laboratories where organic chemistry could be studied—that of Liebig at Giessen, and that of Dumas in Paris. Stas chose the latter, and determined to continue the study of phloridzine in the laboratory of Dumas. Permission so to do was obtained after much difficulty, and the completion of the investigation of phloridzine called forth from Berzelius the following criticism: "We may expect much of a savant who enters the field of science with such a piece of work."

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[1] Abstracted from the address of Prof. A. W. v. Hoffman: Ber. d. chem. Ges. **25**, 1. See also note, This Journal **13**, 430.

That Dumas recognised the ability of his pupil is evident, for the next work of Stas was in conjunction with his teacher—a study of the action of soda-lime upon the alcohols. In the course of this work they applied the method of fusion with caustic potash to a large number of substances, showing that in every case the alcohol yielded the corresponding acid. That fusel-oil should yield an acid identical with the natural valeric acid was at that time of particular interest. Dumas and Stas made determinations of the vapor-density and molecular weight of valeric acid, and, from the fact of its formation from fusel-oil, concluded that the latter must be an alcohol, a view they were able to establish by the preparation of valeric aldehyde from fusel-oil by oxidation.

Their next work in common was the celebrated determination of the atomic weight of carbon, carried out with a care that can hardly be excelled. Berzelius had accepted the figure 12.24, based upon an investigation conducted by himself with Dulong; the work of Dumas and Stas led to the adoption of the figure 12, and this change they justified by careful analyses of carbon compounds of known composition.

An important result of this work was that, with the simple atomic weights $H = 1$, $C = 12$, $N = 14$, $O = 16$, Prout's Hypothesis—then nearly forgotten—was revived. Stas undertook a revision of the atomic weights of many elements, with the firm conviction that the figures obtained would, as in the case of carbon, prove to be whole multiples of the atomic weight of hydrogen. At the end of this his most famous work—an investigation requiring many years for its completion—he declared the hypothesis "all pure illusion." The work of preparation for these studies was full of difficulty: to obtain glass and porcelain which would withstand the action of chemical reagents was almost impossible. To prepare pure compounds from which the atomic weights could be deduced, new methods had frequently to be devised and proved reliable. Stas followed next with his masterly work upon the question of the invariable composition of chemical compounds. He showed that the proportions in which elements unite are for a given compound absolutely definite, and are determined by the nature of the combining elements, and in no way by outside influences, such as pressure or temperature. The atomic weights deduced by him are the following [$H = 1.000$]: $Li = 7.004$, $N = 14.009$, $O = 15.960$, $Na = 22.980$, $Cl = 35.368$, $K = 39.040$, $Br = 79.750$, $Ag = 107.660$, $I = 126.533$. No serious attempt has since been made to revive Prout's hypothesis.

Stas' last great investigation was undertaken with the view of deciding upon the trustworthiness of the statement of Lockyer, that the spectra of the metals of the alkaline earths are changed at high temperatures, whence it was concluded that these metals are not true elements. Stas spent eleven years in preparing pure compounds of silver, sodium, potassium, lithium, calcium, barium, strontium, and thallium, and in repeating Lockyer's experiments with these preparations. He showed that even at the melting-point of iridium (2200°–2500°) the spectra remained unchanged. The important studies made at this time on the spectra of the metals and that of the sun are to be found in an address, "De la nature de la lumière solaire," delivered before the Belgian Academy of Sciences.

Among Stas' minor work may be mentioned the method for the determination of the presence of alkaloids, as in cases of poisoning.

Stas was for twenty years professor in the Military School at Brussels, and was at one time connected with the mint. The fiftieth anniversary of his membership in the Belgian Academy was celebrated in 1891. He died full of years and honors, all Europe having united to show its appreciation of a life devoted to the highest interests of science.

At the meeting of the Belgian Academy of Sciences, March 6, 1892, Professor W. Spring presented a report upon the posthumous scientific papers of Stas.[1] Of these, about 1500 pages had proved to be of value. These would naturally fall into three important treatises. The first, with the title "On Silver," was called forth by the well-known investigation of Dumas, upon the power of silver to occlude gases, as well as by the doubt cast upon the conclusions drawn by Stas with regard to the value of Prout's hypothesis. With the greatest pains Stas prepared absolutely pure silver, in which no occluded gas nor any trace of other foreign matter could be detected. The metal could even be volatilised at the melting point of iridium without giving evidence of the slightest trace of sodium when examined with the spectroscope. The atomic weight of silver was still to be represented by the figure which had been determined by Stas as the result of his earlier investigation. The objections of Dumas in no respect took away from the value of Stas' former work.

The second treatise had to deal with the subject referred to above in connection with the mention of Lockyer's hypothesis.

The third treatise was on a fresh determination of the stoichiometrical relation between silver chloride and potassium chloride. The fact that he would be able to conduct the investigation with absolutely pure material was a strong incentive to undertake the work, laborious as it promised to be. Twelve different determinations agreed with one another in the most astonishing way. Although the atomic-weight determinations—as, for example, of barium, calcium, strontium, and thallium—were not included, yet these last researches of the great analyst will be gratefully welcomed, since not only do they introduce to us a mass of new material of value for the solution of important questions, but they are and must ever remain a standard for exact chemical investigation.

E. R.

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[1] From the Chemiker-Zeitung, March 12, 1892.

Hermann Kopp.

Close upon the death of Stas has followed that of Hermann Kopp. The lives of the two men furnish material for an interesting comparison. Both were throughout life devoted with singleness of purpose to the study of chemistry, yet in different ways. Kopp will always be especially remembered on account of the infinite pains with which he has examined into the records of the work of ancient Philosopher and mediæval Alchemist, the Phlogistonist of former centuries and the Chemist of this, and the zealous care with which he has endeavored once for all to record their claims to the gratitude of later ages; while Stas, with equal patience and marvellous skill, has placed on a firm foundation those fundamental laws of chemical science upon which all future investigations must, at least in great degree, ultimately lean for support. Not that Kopp was a student of the history of chemistry only, but his achievements in that field were so remarkable as to throw rather into the background his only relatively less important experimental investigations.

Kopp was born in 1817. His father was a physician, a man of unusual ability, with an intense interest in scientific knowledge, which was inherited by his son. The latter entered Heidelberg to study under the direction of Gmelin, and from thence moved to Marburg, from which university he was graduated as doctor in 1838. His next move was to Giessen, where the life-long friendship which existed between Liebig and himself was developed. Wöhler, too, soon after joined them, as well as many others who have given evidence to the world of the masterful influence of Liebig over all who approached him. Kopp's work soon began to be concentrated in the department of physical chemistry. In 1841 he was made Privatdocent, and in 1843 Professor in the University, and in Giessen he remained until 1863, when he accepted a professorship in Heidelberg. From this post he could never be enticed away; his devotion to his friends—a life-long characteristic of the man—as well as the charm of life in the romantic old city, always made him strong to refuse the offers made by other universities, and in Heidelberg it was that he died.

Kopp may be considered the pioneer in certain departments of chemical research. Thus his name will always be connected with the development of our knowledge of the dependence of the physical properties of substances upon their chemical composition. His researches upon the specific volume of elements and compounds are perhaps the most famous. Among others might be mentioned his study of the relation between boiling points and chemical composition in the hydrocarbons and their derivatives; his investigation of specific heat and the changes in the volume of substances under the influence of heat, and on melting; his research into the relation of crystalline form to specific volume.

In the last he established the fact that isomorphous substances, with few exceptions, not only show, as Mitscherlich had proved, similar chemical composition, but also the same molecular volume. Kopp was also one of the first rightly to explain the abnormal vapor-densities characteristic of ammonium chloride, phosphorus pentachloride, chloral hydrate, etc.

Hermann Kopp possessed in a remarkable degree the power of acquiring a knowledge of languages: this talent he applied most successfully in his researches in the history of chemistry, afterwards to be given to the world in the famous "Geschichte der Chemie." It is unnecessary to commend the immense labor and absolute thoroughness which its author employed in the preparation of this great work; suffice it to say that it forms the groundwork upon which our present histories of chemistry are all based, and that it probably will always be regarded as a masterpiece in the department to which it belongs. Although published fifty years ago, no revised edition has since appeared; the many monographs, however, which its author has from time to time composed are known to have been intended as chapters in a second edition.

Much of Kopp's work was that of an editor. On the death of Berzelius in 1848 he joined Liebig in the publication of the Jahresbericht. This post of editor he held in common with Liebig until 1857, when the latter withdrew, and afterward with Will until 1862. In the year 1851 he joined Liebig and Wöhler in the editorship of the Annalen, after that journal had been in course of publication nearly twenty years. From that time until his death he was a member of the editorial staff, and as such his name appears on the title-pages of fully two hundred successive volumes.

At the meeting of the German Chemical Society, on February 22d, Prof. v. Hofmann delivered a touching address[1] in memory of Hermann Kopp. The writer of this notice has made use in its preparation of certain details there given. W. W. R.

T. Sterry Hunt.

Dr. T. Sterry Hunt died in New York, February 12, 1892, in his 74th year. He studied chemistry at Yale and was in 1845 made Assistant to Prof. Silliman. In 1847 he was appointed chemist and mineralogist to the Geological Survey of Canada. From 1856 to 1872 he was Professor of Chemistry at Laval University at Quebec and at McGill University at Montreal, successively. From 1872 to 1878 he occupied the position of Professor of Geology at the Massachusetts Institute of Technology. In 1881 the degree of LL. D. was conferred upon him by the University of Cambridge.

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[1] Ber. d. chem. Ges. **25**, 505.

The most valuable of Dr. Hunt's scientific writings may be divided into two groups: (1) those published when a member of the Geological Survey of Canada, and (2) his more or less speculative chemical papers. In the latter he early showed a sympathy with the aims of Gerhardt, and in a series of articles in the American Journal of Science enthusiastically advocated the methods used by the French chemist in his efforts to systematise the classification of chemical substances. In his endeavors to extend the views of Gerhardt he showed himself considerably in advance of most of the chemists of his time. Among his more important chemical papers may be mentioned his "New Basis for Chemistry," "Theory of Chemical Change and Equivalent Volumes," "Chemical and Geological Essays," "Solution and the Chemical Process," "The Foundations of Chemistry," "Mineral Physiology," etc., etc.

In all his speculations he was inclined to take a radical position, and although many of his conclusions would seem to have been justified by the facts, yet it must be remembered that his opinions were frequently characterised by recklessness and narrowness of view.

During the last few years the decline of his health has necessitated his withdrawal, at any rate to a great extent, from active scientific discussion.
W. W. R.

Wilhelm Dittmar.

Wilhelm Dittmar, Professor of Chemistry in the Technical College at Glasgow, died February 9, 1892. He was born in 1833 in Hesse, entered Bunsen's laboratory in 1857, and, after serving some while as assistant, moved to England to occupy a similar position in the laboratory of Roscoe when the latter was appointed to the professorship in the Owens College, Manchester. Between 1861 and 1869 Dittmar served Playfair in the same capacity, after which he returned to Germany. Three years later he became assistant to Professor Crum Brown, was then appointed to a professorship in the Owens College, and, finally, accepted the position of Professor of Chemistry in Glasgow.

Two of Dittmar's more important investigations were the study, with Roscoe, of the chemical relations existing between hydrochloric acid and water, and that upon the process of distillation *in vacuo.*

On the Preparation of Formic Acid.

If in the manufacture of formic acid the mixture of oxalic acid and glycerin is heated on the water-bath, the operation is a very slow one, but on heating but a few degrees above the boiling-point of water the yield in a given time is quite satisfactory. Equal quantities of glycerin and oxalic acid are put into a retort or distilling-flask and this placed in an oil-bath which is heated to 120°. The temperature of the mixture rises slowly to 105°–107°, and there remains for quite a time, while formic acid distils over. It then rises to 112°, again shows a tendency to remain constant, and then again rises. When it reaches 115°, the mixture should be allowed to cool to 65° or 70°, the same quantity of oxalic acid added, again heated, and so on. After the third or fourth addition of oxalic acid, 55 per. cent. formic acid distils over in theoretical quantity and, if the temperature of the oil-bath is kept below 125°, this acid is free from allyl alcohol and cannot be distinguished from the acid prepared at a lower temperature. In my work I used 300 grams of glycerin in a retort or flask of 1000–1200 cc. capacity. With the water-bath less than 100 grams dilute formic acid were obtained, whereas with the oil-bath 900 to 1200 grams oxalic acid were used daily, yielding the second day 550 to 775 grams formic acid, sp. gr. 1.135. FELIX LENGFELD.

From a letter of Dr. Wolcott Gibbs to the Editor.

"Prof. Barker has directed my attention to the fact that in my note on the electrolytic determination of metals as amalgams,[1] the date on which my paper was read before the National Academy of Sciences is given as October, 1883, while the records of the Academy show that the date was November, 1880. The inaccurate statement in my friend Prof. Edgar F. Smith's work is not due to any negligence on his part, but simply to the fact that his information was derived from the Zeitschrift für analytische Chemie and the Chemical News. The fact is that I am myself to blame for neglect to publish a full and complete statement."

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[1] This Journal **13**, 510.

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A REDETERMINATION OF THE ATOMIC WEIGHT OF CADMIUM.

By H. N. Morse and H. C. Jones.

The fractional distillation of metals in a vacuum for the purpose of obtaining pure material for atomic weight determinations, which was first employed in this laboratory by Morse and Burton[1] in their work upon the atomic weight of zinc, was found to be as successful when applied to magnesium and cadmium as it had been with zinc. It was therefore decided to employ it in a redetermination of the atomic weights of those metals also. The work upon magnesium was undertaken by Burton and Vorce,[2] that upon cadmium by the authors of this paper.

At first we only intended to employ the very simple and direct method which had been used in the case of zinc and magnesium, *i. e.* the conversion of the metal into nitrate and then into oxide; but when our work was well advanced, there appeared a paper on the atomic weight of cadmium by Partridge,[3] who had also employed the distillation process for the purification of his metal. As there was some discrepancy between the results obtained by Partridge and by ourselves, we determined to extend the work so as to include one of the methods which had been used by him. Of the three methods used by Partridge, *i. e.* the conversion of the oxalate into oxide, the reduction of the sulphate to sulphide and the conversion of the oxalate into sulphide, the first was selected as probably the best, because it is the simplest and because it gives somewhat more directly the relation of cadmium to oxygen. The uncertainties pertaining to the results obtained by all three of these methods, which are due to the fact that the question of the true atomic weights of carbon and sulphur is involved, have been discussed by Clarke.[1]

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[1] This Journal **10**, 311.

[2] This Journal **12**, 219.

[3] Am. J. Sci. **40**, 377.

The material employed for the preparation of pure metal was obtained from Schuchardt. It was designated by him as "cadmium met. puriss. galv. reduc." This was placed in a combustion tube of glass and heated for a long time in a current of hydrogen, which had been purified by washing with both acid and alkaline solutions of potassium permanganate. In this way it was converted from the form of a powder into bars suitable for distillation in a vacuum. The subsequent treatment of the metal was the same as that employed for the purification of zinc.[2]

Partridge found his material pure after a second distillation, but we were much less fortunate. We could not satisfy ourselves that the metal was entirely free from arsenic until it had been five times redistilled.

It was then redistilled a sixth time. In each of the last two distillations the metal was kept for not less than twenty hours at a temperature just above the melting-point, with the expectation that if traces of arsenic were still present we should be able to find it in the thin incrustation which always collects upon the glass in the cooler end of the tube. In the last distillation nothing but cadmium was found in this incrustation. The sixth distillate, which was the material employed in this work, was examined spectroscopically by Professor Rowland and found to be free from all impurities which can be detected by that method.

The nitric acid used for dissolving the metal was purified as in the case of zinc,[3] by distilling the diluted acid from a flask against a large platinum dish and collecting it in a smaller one of the same metal. It gave no residue on evaporation.

The arrangement of the crucibles in which the metal was dissolved and finally weighed as oxide was similar to that employed in the determination of the atomic weight of zinc above referred to. It consisted of a small porcelain crucible, on the edge of which were placed short U-shaped platinum wires, to prevent the lid from adhering to the crucible and to allow the vapors of oxides of nitrogen to escape, and a larger porcelain crucible in which the smaller one was placed. The glaze upon the outside of the larger crucible was removed by means of hydrofluoric acid, to prevent sticking when heated to a high temperature. These crucibles were weighed together and never separated during a determination. A second pair of crucibles of the same sizes and as nearly as possible of the same weights, but slightly lighter, was used as a tare. The crucibles which served as a tare were prepared in the same manner as the others. The glaze was removed from the outside of the larger one, while the inner one was furnished with platinum wires of the same weight as those of the first pair. The weight of the tare was made equal within less than a tenth of a milligram to that of the first pair, by adding to it small fragments of the same kind of porcelain. Both sets were treated as nearly as possible in the same manner. Whenever acid was added to one, an equal volume was placed in the other. They were likewise heated in every case to the same temperature and for the same length of time.

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[1] This Journal **13**, 34.

[2] Loc. cit. We are much indebted to Dr. W. V. Metcalf, who prepared the pure metal.

[3] Loc. cit.

This method of weighing the containing vessels by means of properly prepared tares which are subjected to the same treatment throughout, was adopted because it rendered our weighings independent of the varying hygroscopic conditions of the air and made their reduction to the vacuum standard unnecessary. Another great advantage derived from this method of weighing by tares is the compensating of any errors due to impurities in the acid or resulting from the prolonged heating of the crucibles. The work at the balance was all done between one and five a. m., and all the precautions mentioned in the article on the atomic weight of zinc were observed. The methods of weighing by vibrations and upon both pans were employed throughout.

To prepare for a determination, the pair of crucibles and the tare were placed upon pieces of unglazed porcelain in larger crucibles of nickel, and heated for half an hour over the blast-lamp. The difference in weight was then ascertained, and the heating and weighing repeated. In every case the first difference found proved to be constant.

A piece of the metal weighing from two to three grams was cut from the bar with a polished and carefully cleaned cold-chisel. The portions which had come in contact with the chisel or with the air were removed with a specially hardened file, which had also been cleaned with alcohol and ether. After weighing, the metal was placed in the inner crucible and treated with an excess of acid. A gentle heat was applied as long as any of the metal remained undissolved. The time required for this part of the operation was from twenty to forty hours. To remove the excess of nitric acid, the crucibles were placed in a porcelain cup which was surrounded by sand, and gently heated until the dried nitrate began to give off red vapors. They were then transferred to a similar bath containing iron filings instead of sand. Here they were heated by a single burner as long as any evidence of decomposition could be observed, and then by triple burners from six to eight hours. Finally, they were heated over the blast-lamp in a bath consisting of a nickel crucible, from two to three hours. To prevent contact between the outer porcelain crucible and the nickel, a piece of unglazed porcelain was placed in the bottom of the bath. To avoid any possible contact of the oxide with reducing gases from the flame, the nickel crucible was tightly forced into a hole cut in a board of asbestus. The heating over the blast was repeated until a constant weight was obtained. Usually three hours of blasting were sufficient, but in some cases four were necessary to bring the oxide to constant weight.

At the temperature of the muffle-furnace the oxide of cadmium attacks porcelain with great energy. For this reason we did not adopt the method employed by Morse and Burton for the final heating of the oxide of zinc. In every case, however, we assured ourselves of the completeness of the decomposition by testing the oxide with pure potassium iodide and hydrochloric acid for the presence of the oxides of nitrogen.

We give below the results of ten successive determinations:

	Cadmium.	Cadmium Oxide.	O = 16. At. Wt. Cd.	O = 15.96. At. Wt. Cd.
I	1.77891	2.03288	112.070	111.790
II	1.82492	2.08544	112.078	111.798
III	1.74688	1.99626	112.078	111.798
IV	1.57000	1.79418	112.053	111.773
V	1.98481	2.26820	112.061	111.781
VI	2.27297	2.59751	112.059	111.779
VII	1.75695	2.00775	112.086	111.806
VIII	1.70028	1.94305	112.059	111.779
IX	1.92237	2.19679	112.083	111.803
X	1.92081	2.19502	112.078	111.798
	18.47890	21.11708	112.0705	111.7905

Maximum, 112.086
Minimum, 112.053
Mean, 112.0705
Difference, .033

The relation established between the total cadmium used and the total oxide found was:

$$\text{Cd} : \text{CdO} = 18.47890 \text{ grams} : 21.11708 \text{ grams};$$
$$\text{or Cd} : \text{O} = 18.47890 \text{ grams} : 2.63818 \text{ grams};$$
$$\text{from which if O} = 16, \quad \text{at. wt. Cd} = 112.0706,$$
$$\text{if O} = 15.96, \quad \text{" " "} = 111.7904.$$

The result obtained agrees more closely with those of von Hauer and Lenssen than with those of any other experimenter.

	Von Hauer. Nine Determinations.	Lenssen. Three Determinations.	Our Work. Ten Determinations.
Max.	112.121	112.304	112.086
Min.	111.796	111.911	112.053
Mean,	111.940	112.067	112.0705
Diff.	.325	.393	.033

Oxalate Method.

Great care was taken to prepare a specimen of oxalic acid which should give no residue on ignition. A large quantity of the acid was agitated with cold water to saturation. The solution thus obtained was evaporated to crystallisation. The product was twice recrystallised in the same manner. It was then heated for two days with a fifteen per cent. solution of hydrochloric acid. The crystals which separated from the acid on cooling were afterwards recrystallised, twice from ninety-five per cent. alcohol and twice from pure ether. The material was then dissolved in pure water and the solution boiled until all odor of ethyl oxalate had disappeared. The crystals which separated from this solution were again crystallised from pure water. The acid thus purified gave no residue after ignition.

All the water used in connection with the oxalate method was purified in the manner previously described for the preparation of pure nitric acid, *i. e.* by condensing its vapor upon cold platinum.

The metallic cadmium was dissolved in pure nitric acid and the excess of acid evaporated off. The nitrate was dissolved in water and treated with a little less than an equivalent amount of oxalic acid in solution. The oxalate which separated after a few moments was collected on a porcelain filter, washed free from nitric acid and dried in an air-bath at 150° C. for twenty hours. In consequence of the hygroscopic nature of the dried oxalate it was necessary to make all weighings in closed vessels. Portions of the salt sufficient for single determinations were placed in glass-stoppered weighing tubes, which had been tared against other similar glasses and dried at 150° C. to constant weight. This last stage of the drying process usually required about fifteen hours. The crucibles used in converting the oxalate into oxide were the same as those previously described. After pouring the oxalate from the tube into the weighed crucibles, the tube and tare were again dried to constant weight at 150° C. This was done to avoid any error resulting from the absorption of water during exposure to the air by the small quantity of oxalate adhering to the inside of the weighing glass. The pair of crucibles containing the weighed oxalate was placed in a larger crucible and heated in an asbestus-covered air-bath. The temperature was increased very slowly until the material began to turn to a brown color on the outer edge. From this point the temperature was kept as nearly constant as possible until the whole mass had become uniformly brown in color. After cooling, the material was completely dissolved in nitric acid and then evaporated to dryness and converted into oxide exactly as in the preceding method.

The table given below contains the results of five successive determinations. The weights of the oxalate given are corrected for the difference in specific gravity between the salt and weights, on the basis of sp. gr. 8.4 for brass and 21 for platinum weights, and sp. gr. 3.31 for oxalate.

	CdC_2O_4.	CdO.	O = 16. C = 12.001. At. Wt. Cd.	O = 16. C = 12.003. At. Wt. Cd.	O = 15.96. C = 11.971. At. Wt. Cd.	O = 15.96. C = 11.973. At. Wt. Cd.
I	1.53937	.98526	112.026	112.033	111.746	111.753
II	1.77483	1.13582	111.981	111.988	111.701	111.708
III	1.70211	1.08949	112.049	112.056	111.769	111.776
IV	1.70238	1.08967	112.051	112.058	111.771	111.778
V	1.74447	1.11651	112.019	112.026	111.739	111.746
	8.46316	5.41675	112.025	112.032	111.745	111.752

Maximum,	112.051	112.058
Minimum,	111.981	111 988
Mean,	112.025	112.032
Difference,	.070	.070

The values assigned to carbon in the last two columns were obtained thus: if when $O = 16$ $C = 12.001$, when $O = 15.96$ $C = 11.971$; if when $O = 16$ $C = 12.003$, when $O = 15.96$ $C = 11.973$.

The ratio established between the oxalate and oxide is:

$CdC_2O_4 : CdO = 8.46316$ grams : 5.41675 grams,

whence, if	$O = 16$	$O = 16$	$O = 15.96$	$O = 15.96$
and	$C = 12.001$	$C = 12.003$	$C = 11.971$	$C = 11.973$
the	at. wt. Cd is	at. wt. Cd.	at. wt. Cd.	at. wt. Cd.
	112.025	112.032	111.745	111.752

Our results agree much more closely with Lenssen's than with Partridge's, as will be seen from the following statements based on the atomic weights of 16 for oxygen and 12.003 for carbon:

Lenssen.	Partridge.	Our Work.
112.043	111.816	112.032

or, on atomic weights of 16 for oxygen and 12.001 for carbon:

Lenssen.	Partridge.	Our Work.
112.036	111.809	112.025

We regard the number 112.0706, which was obtained by converting weighed portions of metal into oxide, as more reliable than the numbers 112.025 or 112.032, obtained by the conversion of weighed quantities of oxalate into oxide.

The first method is exceedingly simple and gives directly the relation of cadmium to oxygen. The substances weighed are not hygroscopic.

The second method is more complicated and involves the question of the true atomic weight of carbon. The oxalate is strongly hygroscopic. Moreover, when it is reduced to oxide by heat there is great danger of loss from reduction to and volatilisation of metal.

Historical.

We append a brief, chronologically arranged account of the determinations of the atomic weight of cadmium which have been made up to the present time. The methods which have been employed are:

1. Conversion of the metal into oxide (Stromeyer).
2. Reduction of the sulphate to sulphide (von Hauer and Partridge).
3. Determination of the chlorine in the chloride (Dumas).

4. Conversion of the oxalate into oxide (Lenssen and Partridge).
5. Determination of bromine in the bromide (Huntington).
6. Conversion of the oxalate into sulphide (Partridge).

1818. Stromeyer: Schweigger's Journ. **22**, 366.

Method: conversion of the metal into the oxide.

100 parts of metal combine with 14.352 parts of oxygen; or Cd : CdO = 6.9677 : 7.9677. O : Cd = 16 : 111.483.

Stromeyer gives no description of his methods; it is therefore impossible to estimate the value of his work.

1857. Von Hauer[1]: Journ. f. prakt. Chem. **72**, 338.

Method: reduction of sulphate to sulphide. Number of determinations, nine.

A total of 64.2051 grams of sulphate gave 44.4491 grams of sulphide.

Whence, if oxygen = 16 and sulphur = 32.059, cadmium = 111.935.

Highest individual result,	112.121
Lowest " "	111.796
Mean of all results,	111.940
Difference between highest and lowest result,	0.325

The sulphate obtained by repeated crystallisations was acidified and treated with hydrogen sulphide. The thoroughly washed sulphide was dissolved in hydrochloric acid, and the cadmium precipitated by ammonium carbonate. The carbonate was carefully washed and converted by heat into oxide. To remove any traces of chloride, the oxide was washed for a long time with boiling water and again ignited. It was then dissolved in dilute sulphuric acid and several times recrystallised. Before each recrystallisation, the sulphate was gently ignited in order to remove any excess of sulphuric acid. The sulphate was finely powdered, dried at about 200° C. and heated, gently at first, but afterwards to redness in a porcelain boat, in an atmosphere of hydrogen sulphide. The sulphide of cadmium was tested in every case for unreduced sulphate.

Von Hauer appears to have taken great care in the purification of his sulphate, and the largeness of the quantities employed in the individual determinations (from six to eight grams) tended to diminish the effect of experimental errors.

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[1] In the eighth determination of von Hauer, the amount of cadmium sulphate used must have been 5.8245 grams, and not 7.8245 grams as given.

The weighing of the anhydrous sulphate and the sulphide in open vessels must have introduced some error. But the most serious source of error, as it appears to us, is the heating of the sulphate in porcelain, to redness, while undergoing reduction. It seems probable that some of the sulphate was decomposed to oxide, which, according to our experience, attacks porcelain with considerable energy at that temperature. The effect of such action would be to lower the atomic weight found.

1859. Dumas: Ann. Chim. Phys. (3), 55, 158.

Method: determination of chlorine in the chloride; number of determinations, six.

A total of 23.0645 grams of cadmium chloride was equivalent to 27.173 grams of metallic silver.

Whence, if chlorine = 35.45 and silver = 107.93, cadmium = 112.322.

Highest individual result,	112.759
Lowest " "	111.756
Mean of all results,	112.241
Difference between highest and lowest result,	1.003

Metallic cadmium was dissolved in boiling hydrochloric acid. The solution was evaporated to dryness and the residue kept in the molten condition in an atmosphere of hydrochloric acid gas for five or six hours. Dumas gives no further particulars as to his procedure. He states, however, that the chloride employed in the first three determinations was of a brown color in places, while that used in the last three was white throughout and perfectly soluble in water, having been prepared from metal supposed to be pure. The results of the first set were: 112.322, 112.347, 112.759; average, 112.476.

The results of the second were: 111.756, 112.135, 112.130; average, 112.007.

It is clear that the first three determinations have little value, while Dumas himself calls attention to a possible source of error pertaining to all of his results. He states that during the heating of the chloride in gaseous hydrochloric acid, a third, a half, or two-thirds of the salt were lost by volatilisation, thus concentrating any less volatile impurities in the residue, which was the material employed in his work.

1860. Lenssen: Jour. f. prakt. Chem. **79**, 281.

Method: conversion of the oxalate into oxide. Number of determinations, three.

A total of 1.5697 grams of oxalate gave 1.0047 grams of oxide. Whence, if oxygen = 16 and carbon = 12.003, cadmium = 112.043.

Highest individual result,	112.304
Lowest individual result,	111.911
Mean of all results,	112.067
Difference between highest and lowest result,	0.393

A solution of repeatedly recrystallised cadmium chloride was treated with an excess of pure oxalic acid. The precipitate was filtered off, very carefully washed, and dried for a long time at 150° C. The weighed salt was decomposed at as low a temperature as possible, in a porcelain crucible. The residue was moistened with pure nitric acid, dried at a gentle heat, and finally strongly ignited.

Lenssen does not state how his nitric and oxalic acids were prepared in the pure condition, neither does he describe any precautions taken to avoid errors resulting from the strongly hygroscopic nature of the dried oxalate. The large differences between the highest and lowest results (nearly .4 of a unit) may have been due to the absorption of water by the oxalate and to the small quantity of material used.

1882. Huntington and Cooke: Proceedings Amer. Acad. **17**, 28.

Methods: (1) determination of bromine in the bromide; (2) determination of the amount of silver required to precipitate the bromine in the bromide.

Number of determinations by each method, eight.

In the first series, a total of 23.3275 grams of cadmium bromide gave 32.2098 grams of silver bromide. Whence, if silver = 107.93 and bromine = 79.95, cadmium = 112.239.

Highest result,	112.290
Lowest result,	112.169
Difference between highest and lowest results,	0.121

In the second series a total of 28.6668 grams of cadmium bromide were equivalent to 22.7379 grams of silver. Whence, if silver = 107.93 and bromine = 79.95, cadmium = 112.245.

Highest result,	112.32
Lowest result,	112.18
Difference between highest and lowest results,	0.14

The commercial metal was dissolved in pure hydrochloric acid, precipitated by hydrogen sulphide, and the sulphide thoroughly washed with hot water. The sulphide was then dissolved in hydrochloric acid, the cadmium precipitated by ammonium carbonate, and the precipitate digested with a large excess of the reagent. The above processes were repeated. Lastly, to remove any traces of chloride, the carbonate was dissolved in pure hydrobromic acid and again precipitated as carbonate. The bromide was prepared by dissolving this carbonate in pure hydrobromic acid and subliming the dried product in a current of pure carbon dioxide.

The experimental part of this work appears to have been carefully done, but the result is strikingly higher than that obtained by any other experimenter, if we exclude the result of Dumas' first series, which, as we have already pointed out, is of but little value.

1890. Partridge:[1] Amer. Jour. Sci. (3), **40**, 377.

Methods: (1) conversion of the oxalate into oxide; (2) reduction of sulphate to sulphide; (3) conversion of the oxalate into sulphide. Number of determinations by each method, ten.

The results of the three series, based on total quantities of materials used and obtained, employing whole numbers for the atomic weights of carbon and sulphur, as was done by Partridge, are given below:

1st series, 12.66368 grams CdC_2O_4 gave 8.10031 grams CdO, at. wt. Cd 111.805.

2d series, 15.93505 grams $CdSO_4$ gave 11.02691 grams CdS, at. wt. Cd 111.786.

3d series, 16.85228 grams CdC_2O_4 gave 12.12906 grams CdS, at. wt. Cd 111.806.

Difference, .02.

But as Clarke[2] has pointed out, if the more probable values for carbon and sulphur are employed in the calculation of the results, the remarkable agreement between the different series disappears. If we employ the numbers 12.001 for carbon and 32.058 for sulphur (Clarke), the results are, for

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[1] The following corrections are to be made in the results as published:

(1) Series: Total cadmium oxide found was 8.10031 grams, and not 8.10027 grams.
(2) Series: Total sulphide found was 11.02691 grams, and not 11.62717 grams.
(3) Series: Sulphide found in eighth experiment, 1.46517 grams, and not 1.45617 grams.

[2] This Journal **13**, 34.

1st series,	111.8036
2d "	111.7271
3d "	111.6054
Difference,	.1982

If we employ the numbers 12.003 for carbon and 32.059 for sulphur (Meyer and Seubert), the results are for,

1st series,	111.816
2d "	111.727
3d "	111.610
Difference,	.206

Of the three methods employed by Partridge, we are prepared at present to speak only of the first. As we have already stated, there are certain unavoidable objections to the method, *i. e.* the hygroscopic nature of the oxalate, the danger of loss of metal during the conversion of the salt into oxide, and the necessity of introducing the atomic weight of another element than oxygen into the calculation. This last objection applies to the second method also, and with double force to the third.

In general we should say that, according to our experience, two rapid distillations, such as are described by Partridge, do not suffice for the purification of the metal.

The following table contains a summary of the results obtained to date. When two values are given for any series of determinations, the first is calculated from the total material used and the total product found; the second is an average of the results of the separate determinations. All the results are calculated on the basis of oxygen = 16, unless otherwise stated:

	Atomic Weight of Cadmium.
1818, Stromeyer,	111.483
1857, von Hauer (S=32.059),	111.935
" "	111.940
1859, Dumas, 1st series (Ag=107.93, Cl=35.45),	112.476
2d " " " " "	112.007
1860, Lenssen (C=12.003),	112.043
" "	112.067
1882, Huntington and Cooke, 1st series (Ag=107.93, Br=79.95)	112.239
2d series, (Ag=107.93, Br=79.95),	112.245

1890,	Partridge, 1st series (C=12, S=32), .	111.805
	2d " " " " " . .	111.786
	3d " " " " " .	111.806
	Partridge, 1st series (C=12.001, S=32.058),	111.8036
	2d " " " " "	111.7271
	3d " " " " "	111.6054
	Partridge, 1st series (C=12.003, S=32.059),	111.816
	2d " " " " "	111.727
	3d " " " " "	111.610
1892,	Morse and Jones, 1st method, . . .	112.0706
	1st " (O=15.96)	111.7904
	2d " (C=12.001)	112.025
	2d " (C=12.003)	112.032
	2d " (O=15.96, C=11.971), .	111.745
	2d " (O=15.96, C=11.973), .	111.752

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

NOTE ON CRYSTALS OF METALLIC CADMIUM.

By George H. Williams.

No reliable crystallographic description of the element cadmium seems thus far to have appeared—a fact due to the difficulty in obtaining suitable material. The crystals submitted to me by Prof. Morse for examination, although not capable of yielding entirely satisfactory results, are nevertheless of much interest.

In 1852 G. Rose noted the fact that distilled cadmium collected at the neck of the retort in drops which solidified as complex polyhedral aggregates,[1] similar to those formed by zinc.[2] In 1874 Kammerer encountered the same aggregates, which he explained as complicated isometric combinations.[3] This opinion was cited in 1881 by Rammelsberg.[4] In 1884 Brögger and Flinck stated that, in their opinion, zinc, magnesium and probably cadmium were, from analogy with beryllium which they had studied, hexagonal and holohedral.[5] This supposition has already been substantiated in the case of the two former elements,[1] while the present material leads to the same result for the last named.

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[1] Pogg. Ann. **85**, 293 (1852).

[2] Ib. Cf. This Journal **11**, 219 (1889).

[3] Ber. d. chem. Ges. **7**, 1724 (1874).

[4] Handb. d. krystallographisch-physikalischen Chemie **1**, 184.

[5] Brögger und Flinck: Zeitschr. f. Kryst. **9**, 236 (1884).

The cadmium crystals were produced, as described in the paper by Prof. Morse and Mr. Jones, in the same manner as were those of zinc and magnesium measured before, viz. by distillation in a vacuum. The appearance of the tubes thus obtained was closely like that in the other cases. The polyhedral aggregates were abundant and reached considerable dimensions. The crystallising force of the cadmium, however, seems to be less, so that the only crystals suitable for measurement were extremely minute. The largest individuals were barrel-shaped, like those of zinc, and resemble little piles of basal plates. Their side planes are not infrequently uneven and bent, probably as the result of the softness and great ductility of the metal.

The most minute crystals alone show pyramidal planes of comparative perfection. These are well suited for a microscopic examination, but their small size renders their measurement on a reflecting goniometer a matter of difficulty. After a careful search two crystals were secured, which, although they had a diameter of only one-third of a millimeter, from their microscopic appearance promised good results. Their planes, however, were found to give compound reflections and a somewhat disappointing variation in corresponding angles.

On the best crystal three zones were measured as follows (normal angles):

Zone I.	Zone II.	Zone III
$0001 : 01\bar{1}1 =$ 62° 35′	$0001 : 10\bar{1}1 =$ 62° 4′	$0001 : 1\bar{1}01 =$ 62° 29′
$0001 : 01\bar{1}0 =$ 89° 50½′,		
$0001 : 01\bar{1}\bar{1} =$ 118° 57′	$0001 : 10\bar{1}\bar{1} =$ 118° 28′	

The second crystal was much less satisfactory, since values for the angle between the base and pyramid, $(0001) : (01\bar{1}1)$, were obtained which varied all the way from 61° 2′ to 63° 43′. These measurements must therefore be regarded as of little or no value. If we average the readings for this angle on the first crystal we obtain 62° 23′, corresponding to the axial ratio $a : c :: 1 : 1.6554$.

A comparison between the axial ratios of the four rhombohedral and four holohedral hexagonal elements gives the following :

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[1] Williams and Burton: This Journal **11**, 225 (1889). Ib. **12**, 225 (1890).

Rhombohedral:
Bismuth, $a : c = 1 : 1.3035$ (G. Rose, 1849).
Antimony, $a : c = 1 : 1.3235$ (Laspeyres, 1875).
Tellurium, $a : c = 1 : 1.3298$ (G. Rose, 1849).
Arsenic, $a : c = 1 : 1.4025$ (Zepharovich, 1875).
Holohedral:
Zinc, $a : c = 1 : 1.356425$ (Williams and Burton, 1889).
Beryllium, $a : c = 1 : 1.5802$ (Brögger, 1884).
Magnesium, $a : c = 1 : 1.6202$ (Williams, 1890).
Cadmium, $a : c = 1 : 1.6554$ (Williams, 1891).

Zinc appears from its axial ratio to belong rather to the rhombohedral group, and this is the only one of the last four elements upon which the faintest indication of any divergence from a holohedral development of all of its forms has been observed. On crystals of this substance there is an occasional rhombohedral alternation of the faces of certain of the pyramids, although the crystals otherwise appear to be holohedral.[1]

The crystals of cadmium, like those of magnesium, show only the three forms $0P$ (0001), P $(10\bar{1}1)$, and ∞P $(10\bar{1}0)$. Brögger and Flinck observed on beryllium the additional forms $\infty P2$ $(2\bar{1}\bar{1}0)$ and $\frac{1}{2}P$ $(20\bar{2}1)$; while upon zinc a large number of forms in the zone of the unit pyramid occur. Not infrequently the cadmium crystals show a tendency toward a hemimorphic development. This is plainly seen when a large number of them are examined together under the microscope. The little barrel-shaped crystals are mostly attached by their sides, and yet one of their ends is often broader than the other. Sometimes they taper nearly to a point, quite like greenockite crystals.

The cohesion phenomena of cadmium are similar to those of zinc, but are still more striking. When a crystal is sharply focused under the microscope and then gently pressed on the side with the point of a needle, an unbroken pyramidal face is seen to suddenly become striated parallel to the basal plane, as though a gliding in the basal section took place. Some of these crystals were kindly examined by Prof. Otto Mügge of Münster, Germany, who has added so much to our knowledge of the cohesion phenomena in crystals. He has written me in regard to his observations as follows: "The cadmium crystals, as far as their gliding phenomena are concerned, behave quite like zinc. If a crystal is carefully loosened and then squeezed with a pair of pincers, it is easy to see that the smooth surface where it was attached to the glass becomes striated parallel to oP (0001), and that at the same time two other sets of striations are produced which meet at an angle of about 85° and intersect the trace of the basal plane at about 47½°. The plane of attachment was selected for observation because it was smoother than the pyramidal faces. In the above case this plane has the position of a steep pyramid, inclined to the base at an angle of about 100°. The oblique sets of striations appear to represent gliding planes parallel to the unit pyramid faces (2P, (10$\bar{1}$2) of Rose), as is the case with zinc. Whether the horizontal striations were due to gliding parallel to the base I could not certainly decide. Many of the crystals appear, when pinched, to be completely overturned, in which cases ordinary bending accompanies gliding, as in the case of gold, etc. This is shown by the fact that both faces and striations become rounded."

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[1] This Journal **11**, 224 (1889). Pl. 2, Fig. 8.

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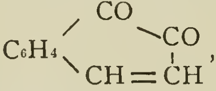
Contribution from the Chemical Laboratory of Clark University, Worcester, Mass.

ON THE ETHERS OF QUINONE-OXIME (NITROSO-PHENOL).

FIRST PAPER.

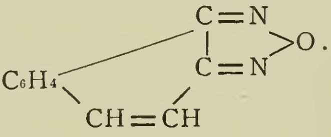
BY J. L. BRIDGE.

Some time ago H. Goldschmidt[1] proved that α-nitroso-β-naphthol and β-nitroso-α-naphthol were both oximes of β-naphthoquinone,



$C_6H_4\left<\begin{array}{l}CO - CO\\ \qquad\quad\;\; |\\ CH = CH\end{array}\right.$, as follows:

1. Both these substances give on treatment with hydroxylamine the same dioxime-anhydride,



$C_6H_4\left<\begin{array}{l}C=N\\ |\qquad >O.\\ C=N\\ CH=CH\end{array}\right.$

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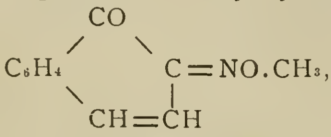
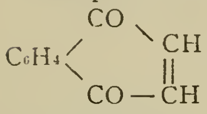
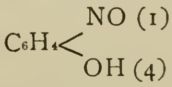
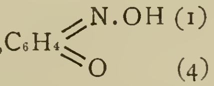
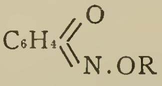
[1] Ber. d. chem. Ges. **17**, 801; **18**, 571 and 2224.

2. The ethers, obtained by treating the silver salts of these two substances with alkyl iodides, give on reduction amido-naphthols, hence the alkoxy groups cannot be present in the form of phenol ethers.

3. β-Naphthoquinone gives with α-methyl-hydroxylamine, CH_3-O-NH_2, a substance, , which is identical with the methyl ether obtained by treating silver β-nitroso-α-naphthol with the methyl iodide.

That para-nitroso-α-naphthol is an oxime of α-naphthoquinone, , is rendered probable by the fact that it is obtained from this quinone by means of hydroxylamine[1] (one molecule); in this case, however, further proofs are wanting. The same is true of ordinary para-nitroso-phenol. The latter substance is at the present time still regarded as a tautomeric compound, *i. e.* it seems to show a twofold chemical behavior, at times reacting as a nitroso-phenol,  $C_6H_4<\begin{matrix}NO\ (1)\\ OH\ (4)\end{matrix}$, and at other times like a quinone-oxime,  $C_6H_4\begin{matrix}= N.OH\ (1)\\ = O\ \ \ \ \ \ \ (4)\end{matrix}$. For this there is, however, no positive evidence, and indeed nitroso-phenol, owing to its instability, has as yet been very little studied. I have therefore undertaken a study of this substance under the direction of Dr. Nef, with the object of obtaining ethers of it; and although both Ter Meer[2] and H. Goldschmidt[3] have stated that they obtained negative results in this direction, it was found that both silver- and sodium-nitroso-phenol react with alkyl iodides and acid chlorides, giving ethers of nitroso-phenol whose constitution was definitely proved to be as follows:  $C_6H_4\begin{matrix}= O\\ = N.OR\end{matrix}$, *i. e.* the ethers are quinone oxime-ethers. It was also found that the benzoyl- and ethyl-carbonic ethers which Walker[4] obtained in 1884 and describes as phenol-ethers,

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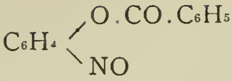
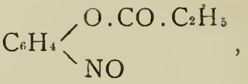
[1] Ber. d. chem. Ges. **17**, 2064. [2] Ibid. **8**, 625. [2] Ibid. **18**, 2226. [4] Ibid. **17**, 400.



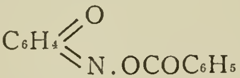
$C_6H_4\langle^{O.CO.C_6H_5}_{NO}$

and



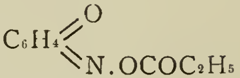
$C_6H_4\langle^{O.CO.C_2H_5}_{NO}$,

are in reality ethers of quinone-oximes,



$C_6H_4\langle^{O}_{N.OCOC_6H_5}$

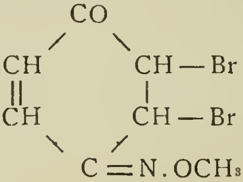
and



$C_6H_4\langle^{O}_{N.OCOC_2H_5}$,

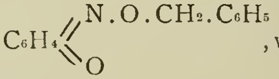
so that at present not a single reaction shown by nitroso-phenol can be construed as tending to show that this substance is a tautomeric compound. The ethers obtained by Walker were made by treating sodic phenolate with amyl nitrite and heating the resulting sodic nitroso-phenolate with benzoyl chloride or with chlorocarbonic ether. Walker supposed these to be real ethers of nitroso-phenol, because the sodium in the first place (sodium phenolate) was bound to the phenol group.

The ethyl and methyl ethers of quinone-oxime described in this paper are very remarkable substances; they no longer resemble nitroso-phenol in the least, but are yellow, strong-smelling substances, very volatile with steam, and show a very close resemblance in every particular to benzoquinone. Like it they form addition-products with the halogens;[1] the methyl ether, for instance, gives a colorless dibromide,



, which is not affected by fuming nitric acid.

The conclusive proof that the ethers obtained are not ethers of nitroso-phenol but of quinone-oxime is as follows: α-benzylhydroxylamine, $C_6H_5.CH_2—O—NH_2$, (one molecule) converts quinone quantitatively into the ether



$C_6H_4\langle^{N.O.CH_2.C_6H_5}_{O}$

, which is identical in every respect with the ether obtained from sodic or silver nitroso-phenol and benzyl chloride.

The results obtained also show that the properties and stability of quinone and its derivatives depend entirely on the negative or positive condition of the molecule,[2] and this explains the entirely different properties of the following substances which are all analogously constituted:

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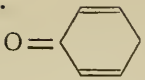
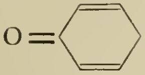
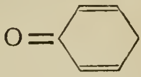
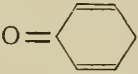
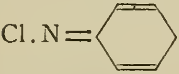
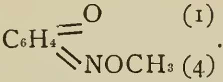
[1] This Journal **12**, 483. Ibid. **13**, 424.

[2] Cf. Nef: Ann. Chem. (Liebig) **266**, 52.

Quinone, =O, yellow, volatile, pungent odor, adds 4 atoms chlorine or bromine; quinone-oxime methyl ether, =N—OCH$_3$, yellow, volatile, strong odor, adds 2 atoms bromine; quinone-oxime benzoyl ether, = N—O.COC$_6$H$_5$, odorless, almost colorless, like nitroso-phenol; quinone-oxime, =NOH, colorless, solutions green, adds 2 atoms bromine with difficulty; quinone-dichlor-diimid, =NCl, colorless, odorless, very stable, does not add bromine.

Quinone-oxime methyl ether, 

$C_6H_4\begin{matrix}=O & (1)\\ \diagdown NOCH_3 & (4)\end{matrix}$

.—The nitroso-phenol used in the following experiments was obtained as follows: 50 grams phenol, 25 grams sodium hydroxide, 45 grams sodic nitrite were dissolved in 1200 cc. of water and the solution cooled to 7°–8°. Thereupon 700 cc. dilute sulphuric acid (1:5) were added gradually, the vessel being cooled and shaken thoroughly during this operation. After two hours the nitroso-phenol which had separated out was filtered off and washed with ice-water, and then purified by dissolving in ether and treating in the cold with animal charcoal. On concentrating the etherial solution nitroso-phenol crystallises out in pale yellow needles which, if dried quickly, can be kept without change.

Silver nitroso-phenol was made by dissolving 1 gram of nitroso-phenol in sodic hydroxide (from 0.16 gram sodium) and pouring into a solution of silver nitrate (1.6 grams) in 300 cc. of water. The gelatinous dark-brown salt, which has been analysed by Ter Meer,[1] was filtered off, well washed, dried on clay plates and then at 75°.

The silver salt thus obtained was suspended in a small amount of absolute ether, and 1¼ times the calculated amount of methyl iodide added, the solution being cooled if necessary. The mixture must not be warmed, and after standing for an hour or longer is filtered and the etherial filtrate allowed to evaporate spontaneously. There is left a dark-brown, tarry mass which is digested with hot ligroin (boiling point 70°–80°), which extracts the methyl ether but leaves the tar behind. The ligroin solution is treated with animal charcoal until it becomes bright yellow in color, and on concentration a substance separates out in flat yellow needles which, recrystallised again, is pure and melts sharply at 83°.

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[1] Ber. d. chem. Ges. 8, 624.

0.1362 gram substance,[1] dried over sulphuric acid in a vacuum, gave 0.3070 gram CO_2 and 0.0664 gram H_2O.

0.1560 gram substance gave 14.3 cc. moist nitrogen at 22° and 748.2 mm.

	Theory for $C_7H_7NO_2$.	Found.
C	61.35	61.46
H	5.11	5.42
N	10.21	10.24

The methyl ether has a strong and pleasant etherial odor, is readily volatile with steam: if not quite pure it, like quinone, decomposes quickly, turning first green and then dark-brown. The substance is very readily soluble in organic solvents and hot water; it dissolves in considerable amount in cold water and ligroin.

This same substance is formed by warming gently a solution of sodic nitroso-phenol (made from nitroso-phenol and sodium ethylate) in methyl alcoholic solution with methyl iodide. The color of the solution changes from brown to dark-red, and a dark-red substance separates out in needles[2] (yield always about 0.2 gram from 1 gram nitroso-phenol taken) which is probably a polymeric nitroso-phenol. It is insoluble in organic solvents, but dissolves in caustic alkalies and ammonia with deep-red coloration, and is precipitated unchanged therefrom by means of acids or carbon dioxide. It does not melt but begins to decompose at about 250°. Repeated analyses were made, but no constant figures were obtained, as the substance seems to burn with enormous difficulty. The following reactions shown by the substance make it probable, however, that it is a polymeric nitroso-phenol: nitric acid (sp. gr. 1.4) converts it quantitatively into 1.2.4.-dinitrophenol[3] (m. p. 114°). Tin and hydrochloric acid reduce it to para-amido-phenol (m. p. 180°), which was further proved by the conversion of this substance into quinone and quinone chlor-imid (m. p. 84.5°).

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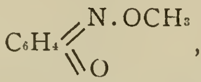
[1] All the analyses in this paper were carried out by mixing the substance with the copper oxide.

[2] Cf. Ter Meer: Ber. d. chem. Ges. 8, 625.

[3] Laurent: Ann. Chem. (Liebig) **43**, 213; Körner: Ztschr. Chem. 1868, 322.

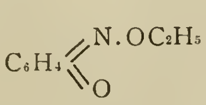
The above alcoholic filtrate contains, besides much tarry matter, quinone-oxime methyl ether, which was obtained by allowing the solution to evaporate spontaneously and extracting the residue with ligroin.

Quinone-oxime methyl ether dibromide,  $C_6H_4\left\langle\begin{matrix}N.OCH_3\\O\end{matrix}\right., Br_2$.—The methyl ether just described, when treated in chloroform solution with bromine (one molecule), is quantitatively converted into a dibromide. The absorption of the bromine is complete in half an hour and no hydrobromic acid is noticed. The solution is then allowed to evaporate spontaneously, and the residue, which is slightly colored, purified by dissolving twice in fuming nitric acid and pouring this solution into ice-water. The substance thus treated is colorless, and crystallises from chloroform in four-sided plates, which when heated begin to soften at 113° and melt completely at 118° without decomposition.

0.2820 gram substance, dried over sulphuric acid in a vacuum, gave 0.2962 gram CO_2 and 0.0676 gram H_2O.

0.1548 gram substance gave 0.1976 gram AgBr (Carius).

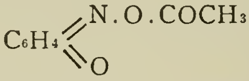
	Theory for $C_7H_7NO_2Br_2$.	Found.
C	28.57	28.64
H	2.36	2.66
Br	53.88	54.26

Quinone-oxime ethyl ether,  $C_6H_4\left\langle\begin{matrix}N.OC_2H_5\\O\end{matrix}\right.$.—This ether is obtained like the methyl ether by treating the silver salt of nitroso-phenol with ethyl iodide. Crystallised from ligroin it is obtained in yellow rhombic or in hexagonal plates, melting at 30° and having a strong etherial odor.

0.1058 gram substance, dried over sulphuric acid in a vacuum, gave 0.2472 gram CO_2 and 0.0608 gram H_2O.

	Theory for $C_8H_9NO_2$.	Found.
C	63.58	63.71
H	5.96	6.38
N	9.27	9.31

The ethyl ether is easily volatile with steam; it dissolves readily in all solvents, but is least soluble in cold water and ligroin, and owing to its low melting-point as well as ready solubility is obtained pure with some difficulty. If impure, it decomposes on standing.

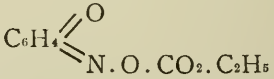
Quinone-oxime acetyl ether,  $C_6H_4\left\langle\begin{matrix} N.O.COCH_3 \\ O \end{matrix}\right.$.—Silver nitroso-phenol, suspended in much absolute ether, reacts quickly on treating with one molecule of freshly distilled acetyl chloride. The etherial filtrate gives a yellow substance in large quantity, which, recrystallised from ligroin (b. pt. 70°–80°), or from a mixture of ligroin and benzene (using animal charcoal), was obtained in light-yellow needles melting at 107°.

0.1898 gram substance, dried over sulphuric acid in a vacuum, gave 0.4046 gram CO_2 and 0.0768 gram H_2O.

0.1864 gram substance gave 14 cc. moist nitrogen at 22° and 750.6 mm.

	Theory for $C_8H_7NO_3$.	Found.
C	58.18	58.14
H	4.28	4.49
N	8.49	8.62

Acetyl-quinone-oxime is but slightly soluble in water; it is odorless, and its etherial and alcoholic solutions are colored green (like those of nitroso-phenol). If dry and finely powdered it causes sneezing.

Quinone-oxime ethyl-carbonic ether,  $C_6H_4\left\langle\begin{matrix} O \\ N.O.CO_2.C_2H_5 \end{matrix}\right.$.—Equal molecules of chloro-carbonic ether and silver nitroso-phenol, suspended in absolute ether, were heated gently for a short time. The ether extract gives a yellow substance crystallising from ligroin in hexagonal plates melting at 110°. It is identical with an ether obtained by Walker.[1]

0.1208 gram substance, dried over sulphuric acid in a vacuum, gave 0.2456 gram CO_2 and 0.0546 gram H_2O.

0.2616 gram substance gave 16 cc. moist nitrogen at 23° and 752 mm.

	Theory for $C_9H_9NO_4$.	Found.
C	55.38	55.45
H	4.62	5.02
N	7.18	7.08

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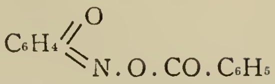
[1] Ber. d. chem. Ges. **17**, 400.

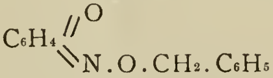
Quinone-oxime benzoyl ether,  $C_6H_4\begin{matrix} /\!/ O \\ \diagdown N.O.CO.C_6H_5 \end{matrix}$.—This ether can be obtained in three ways: by treating the dry sodium or silver salt of nitroso-phenol with benzoyl chloride, or by shaking an alkaline solution of nitroso-phenol with benzoyl chloride[1] (best method). The resulting product is purified by repeated crystallisation from alcohol, and obtained thus in light-yellow needles melting at 172°–174°. The alcoholic solutions possess a green color, but not so marked as those of nitroso-phenol or its acetyl ether. This ether is identical with Walker's[2] product, who gives the melting point 168°–175°.

1. 0.2584 gram substance, dried at 100°, gave 13.5 cc. moist nitrogen at 21° and 758 mm. (from Ag salt).

0.1496 gram substance, obtained by Baumann's reaction, gave 0.3752 gram CO_2 and 0.0590 gram H_2O.

2. 0.1996 gram substance, obtained by Baumann's reaction, gave 10.7 cc. moist nitrogen at 20° and 758.3 mm.

	Theory for $C_{13}H_9NO_3$.	Found.	
		I.	II.
C	68.72	68.40	...
H	3.97	4.31	...
N	6.17	6.08	6.26

Quinone-oxime benzyl ether,  $C_6H_4\begin{matrix} /\!/ O \\ \diagdown N.O.CH_2.C_6H_5 \end{matrix}$.—Silver nitroso-phenol, suspended in absolute ether, is heated for several hours with benzyl chloride (¾ molecule), until the smell of the latter substance has disappeared. The etherial filtrate gives a yellow substance which, recrystallised from ligroin, is obtained in yellow rectangular or rhombic plates melting at 63.5° The same substance is formed by heating sodic nitroso-phenol in alcoholic solution with benzyl chloride.

0.1514 gram substance, dried over sulphuric acid in a vacuum, gave 0.4068 gram CO_2 and 0.0770 gram H_2O.

0.3300 gram substance gave 19 cc. moist nitrogen at 20° and 762.2 mm.

	Theory for $C_{13}H_{11}NO_2$.	Found.
C	73.24	73.28
H	5.17	5.64
N	6.57	6.60

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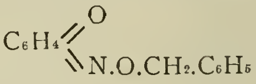
[1] Ber. d. chem. Ges. **21**, 2744.

[2] Ibid. **17**, 400.

Benzyl quinone-oxime is insoluble in water, but readily soluble in all organic solvents except ligroin. It has no smell. Treated with tin and hydrochloric acid, it is converted into para-amidophenol, while much benzyl chloride is also formed. The para-amido-phenol obtained was also converted into quinone-chlorimid (m. p. 84°). This shows that the benzyl group is bound to oxygen, but not in the form of a phenol ether. The conclusive proof that the benzyl ether has the constitution  $C_6H_4\begin{matrix}{/\!/O}\\{\backslash\!\backslash N.O.CH_2.C_6H_5}\end{matrix}$ is as follows:

The same substance is obtained quantitatively by treating quinone (one gram) dissolved in 250 cc. of water with the calculated amount of α-benzyl-hydroxylamine hydrochloride,[1] $C_6H_5.CH_2.O.NH_2, HCl$, dissolved in water containing a few drops of hydrochloric acid. The separation of the ether begins immediately: the reaction is complete in 12 hours, and the product obtained practically pure; yield, 1.95 grams (theoretical, 1.98 grams).

Recrystallised once from ligroin it is obtained in yellow plates melting at 63.5°, and identical in every respect with the above ether obtained from silver or sodium nitroso-phenol.

0.1760 gram substance, dried over sulphuric acid in a vacuum, gave 0.4700 gram CO_2 and 0.0866 gram H_2O.

0.2302 gram substance gave 13 cc. moist nitrogen at 20° and 761.8 mm.

	Theory for $C_{13}H_{11}NO_2$.	Found.
C	73.24	72.84
H	5.17	5.35
N	6.57	6.48

WORCESTER, *April* 19, 1892.

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[1] Behrend and Leuchs: Ann. Chem. (Liebig) **257**, 205.

THE COMPOSITION OF THE EXPLOSIVE COPPER AND SILVER COMPOUNDS OF ACETYLENE.[1]

By Edward H. Keiser.

One of the earliest observations made upon the properties of acetylene was that when it is passed into ammoniacal solutions of cuprous chloride and silver chloride, precipitates are formed which after drying are extremely explosive.

As long ago as 1858 Quet[2] observed that when electric sparks are passed through liquid alcohol, a gas is obtained which consists of carbon monoxide and a hydrocarbon. The hydrocarbon gave a brown precipitate with ammoniacal cuprous chloride and a yellow precipitate with ammoniacal silver chloride. He also noticed that these precipitates after being dried are explosive, but he appears to have made no attempts to determine their composition.

Among those who subsequently worked with these compounds were Böttger,[3] Vogel and Reischauer,[4] Torrey[5] and Crova.[6]

Berthelot,[7] however, appears to have been the first to attempt to express the composition of these substances by means of formulas. He concluded from his experiments that they contained radicles consisting of carbon, hydrogen and copper in the one case, and carbon, hydrogen and silver in the other, and that in each case these radicles were in combination with oxygen. Thus the copper precipitate he called *cuprosacetyl oxide*, and gave to i the formula $(C_2Cu_2H)_2O$. The silver precipitate was called *argentacetyl oxide*, and to it was given a similar formula, $(C_2Ag_2H)_2O$.

Other investigators who have studied these compounds have come to different conclusions in regard to their composition. Thus Reboul[8] assigns to the copper precipitate the formula C_2HCu, while for the silver compound he writes the formula $(C_2HAg)_2Ag_2O$. Miasnikoff[9] analysed the silver compound and found that his results agreed best with the formula $C_2H_2Ag_2$. The latest work upon this subject has been done by Blochmann,[10] who analysed both the silver and copper precipitates and concluded that their composition is best represented by the formulas $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$.

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[1] Read at the meeting of the Franklin Institute, Feb. 16, 1892.

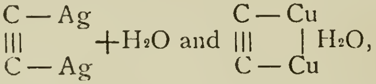
[2] Compt. rend. **46**, 903; Ann. Chem. (Liebig) **108**, 116.

[3] Jsb. Chem. 1859, 219. [4] Ibid. 1858, 208. [5] Ibid. 1859, 222. [6] Ibid. 1862, 442.

[7] Ann. Chem. (Liebig) **123**, 216; **138**, 245; **140**, 314.

[8] Ibid. **124**, 267; Compt. rend. **54**, 1227. [9] Ibid. **118**, 330. [10] Ibid. **173**, 176.

These formulas have found their way into the text-books and appear to have been generally accepted. Some authors write the formulas as above, apparently regarding the compounds as made up of molecules of acetylene and of cuprous oxide in the one case, and of acetylene and silver oxide in the other. More recently there seems to be a tendency to regard them as metallic substitution-products of acetylene, and in some of the later works[1] it is stated that perhaps the constitution of these compounds may be represented by some such formulas as:



$$\begin{array}{l} C-Ag \\ \,||| \\ C-Ag \end{array} + H_2O \text{ and } \begin{array}{l} C-Cu \\ \,||| \\ C-Cu \end{array} \mid H_2O,$$

$$\text{or } HC\equiv C-Ag-AgOH \text{ and } HC\equiv C-Cu-CuOH.$$

In view of the uncertainty, therefore, that prevails in regard to the composition of these substances, it seemed desirable to undertake new experiments to determine if possible their true composition, and in anticipation of what follows it may here be stated that it was found as a result of this work that in pure dry condition neither of these bodies contains hydrogen or oxygen, that they are simple carbides of the metals, and that their composition must be represented by the formulas C_2Ag_2 and C_2Cu_2.

Preparation and Analysis of the Silver and Copper Compounds.

In all the experiments the acetylene was made by the action of alcoholic caustic potash upon ethylene bromide. The gas was passed through a second portion of hot alcoholic potash to remove vinyl bromide and was then washed with absolute alcohol. Thereupon the acetylene was passed into the ammoniacal solutions of cuprous chloride, or of silver nitrate. As the copper compound oxidises rapidly in the air, and the silver compound turns black in the light, special precautions had to be taken in washing and drying the precipitates. The washing was carried on in tall cylinders from which the air was removed by a current of carbon dioxide. The precipitates were washed by decantation, first with water to which ammonia had been added, afterwards with pure water and finally with alcohol and ether. Finally, the precipitates were drained on a funnel by means of the filter-pump, and then quickly transferred to sulphuric acid desiccators which were in connection with a mercury air-pump. The air was then removed and the precipitates allowed to remain until thoroughly dry. The desiccator containing the silver precipitate was protected from the light, and the silver compound when dry was of a snow-white color.

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[1] Watt's Dictionary, Morley and Muir, **1**, 43; Organische Chemie, V. Meyer and Jacobson, **1**, 456. Ramsay, "Systematic Chemistry," writes the formula of the silver compound $HC\equiv CAg$.

The silver compound was analysed by treating weighed quantities in a porcelain crucible with dilute hydrochloric acid and evaporating to dryness: this was repeated until the weight remained constant. The following results were obtained:

Specimen *A*	0.2588	gram	gave	0.3075	gram	AgCl.
	0.3910	"	"	0.4640	"	AgCl.
Specimen *B*	0.3347	"	"	0.3971	"	AgCl.
Specimen *C*	0.1217	"	"	0.1449	"	AgCl.

	A	*B*	*C*
Percentage Ag—	89.44 89.33	89.31	89.62

Preparations *A* and *B* were dried in a vacuum at ordinary temperatures, while preparation *C* was dried in a vacuum at 100°.

Mean value of silver found = 89.45 per cent.

Berthelot's	formula,	$(C_2Ag_2H)_2O$,	requires	86.74	per	cent.
Reboul's	"	$(C_2AgH)_2Ag_2O$,	"	86.74	"	"
Miasnikoff's	"	$C_2H_2Ag_2$,	"	89.25	"	"
Blochmann's	"	$C_2H_2Ag_2O$,	"	83.71	"	"
		C_2Ag_2	"	89.99	"	"

The percentage of silver found indicates that the formula must be either $C_2H_2Ag_2$ or C_2Ag_2.

To determine whether the compound contains hydrogen, a weighed quantity of the substance was exploded in a vacuum. 0.2225 gram of the substance was placed in a glass tube closed at one end, the open end was filled through a distance of several inches with a long plug of glass-wool and was then connected with a mercury air-pump. After a perfect vacuum had been obtained the substance was gently heated. A bright flash of light indicated that decomposition had taken place. On again exhausting the tube, scarcely any gas at all was obtained; after exhausting the tube for a long time, a volume of gas measuring a cubic centimeter had collected, but on bringing this gas in contact with caustic potash it nearly all disappeared, showing that it was largely carbon dioxide. If the compound had contained hydrogen, as is indicated by the formula $C_2H_2Ag_2$, it should have given on decomposition about 24 cubic centimeters of gas. The tube containing the decomposed compound was again weighed after the explosion; the weight had remained unchanged. An examination of the black residue left in the tube showed that it consisted of carbon and finely divided silver.

These experiments seem to prove beyond a doubt that the silver compound of acetylene contains only silver and carbon and that its composition is represented by the formula C_2Ag_2.

The copper compound was prepared, washed and dried in the way that has already been described in connection with the silver compound. The percentage of copper in the compound was at first determined by treating a weighed quantity in a crucible with nitric acid and evaporating to dryness, and heating and weighing the copper oxide formed. It was found difficult to obtain accurate results in this way: more or less copper was volatilised although great pains were taken to heat the copper nitrate very gradually. It was found better to dissolve the substance in dilute nitric or hydrochloric acid and to precipitate the copper oxide with caustic soda. By this method the following results were obtained:

Specimen A.

0.3130 gram gave 0.3153 gram CuO = 80.43 per cent. Cu,
0.4085 " " 0.4151 " " = 81.14 " " "

Specimen B.

0.0726 gram gave 0.0735 gram CuO = 80.84 per cent. Cu.
0.2120 " " 0.2131 " " = 80.27 " " "

Another portion of specimen *B* was dried in a vacuum at a temperature of 100°. 0.2490 gram of the dried compound gave 0.2521 gram CuO = 80.90 per cent. Cu. It was noticed that in every case when the copper acetylide was dissolved in acids that small black flakes remained undissolved. An examination of these flakes showed that they consist of carbon. Every specimen of the copper precipitate that was prepared was found to contain some free carbon. The silver compound, on the other hand, was free from carbon. All attempts to prepare the copper acetylide free from carbon have failed. It appears that when acetylene is conducted into a cuprous solution, and air or oxygen is present in small quantity and the cuprous compound is thereby oxidised to the cupric condition, there is formed the red cuprous acetylide, but at the same time some of the hydrogen of the acetylene or the copper of the precipitate is oxidised and carbon remains behind. For the purpose of obtaining a pure compound other methods of preparation were tried. Acetylene was passed into water in which finely divided cuprous chloride was suspended. There was an abundant formation of the red compound, but this was also found to contain carbon, and it was impossible to remove all cuprous chloride from the precipitate by prolonged washing with ammonia. Acetylene passed into a solution of cuprous oxide in ammonia also gives the red precipitate, but as the cuprous oxide slowly oxidises, the precipitate carries the copper oxide down with it. This specimen contained besides the copper oxide some free carbon. The copper acetylide is so voluminous when first formed that it reminds one of the appearance of ferric and aluminium hydroxides, and like these it carries down small quantities of substances that may be in solution. Owing to the ease with which the moist copper acetylide oxidises in the presence of air, it is extremely difficult to remove these substances by washing.

The purest specimen was obtained by the reaction of acetylene upon cuprous hydroxide suspended in water. The yellow hydroxide is readily converted into the red cuprous acetylide. Even this precipitate contained a trace of carbon. It was analysed by dissolving a weighed quantity in dilute hydrochloric acid. The free carbon was removed by filtration, and in the filtrate the copper, after oxidation, was determined as oxide. The weight of free carbon was deducted from the weight of compound taken.

0.1527 gram gave 0.1593 gram $CuO = 83.36$ per cent. Cu.
0.0699 " " 0.0735 " " $= 83.96$ " " "
Berthelot's formula, $(C_2Cu_2H)_2O$, requires 79.3 per cent. Cu.
Blochmann's " $C_2H_2Cu_2O$, " 75.1 " " "
Reboul's " C_2HCu, " 71.7 " " "

The formula C_2Cu_2 requires 84.08 per cent. Cu. The analyses indicate that the formula of the compound is C_2Cu_2. The somewhat lower value of copper obtained is due to the great difficulty of obtaining the compound in pure condition, owing to its tendency to carry down substances that may be in solution. The presence of a small quantity of copper oxide in the compound would be sufficient to account for the difference noticed.

To determine whether the substance contained hydrogen or water, a weighed quantity of the carefully dried compound was exploded in a vacuum, by the method described under the silver compound. No hydrogen was obtained, nor did the tube change in weight. If water had been present it would have evaporated under the conditions used to bring about decomposition, and its weight could have been determined by the loss in weight of the tube.

The conclusions reached as a result of these experiments are that the composition of the copper and silver compounds of acetylene is best represented by the formulas

$$C_2Cu_2 \text{ and } C_2Ag_2.$$

The silver compound can readily be obtained in pure condition by the process of preparation described above. The copper compound, on the other hand, is nearly always impure; it contains free carbon, and owing to its colloidal nature carries down both cuprous and cupric salts which may be present.

The hydrogen of acetylene is evidently of an acid character and replaceable by metals. Berthelot has shown that when sodium and potassium are heated in a current of acetylene, the compounds C_2Na_2 and C_2K_2 are formed; and indeed it was by the decomposition of the latter substance, obtained in the preparation of metallic potassium, that E. Davy in 1836 first obtained the hydrocarbon. While the acetylene derivatives of the alkali metals can thus be obtained at high temperatures in the absence of water, those of the metals that do not decompose water can be readily formed at ordinary temperatures and in the presence of water. Thus the cuprous and silver derivatives are formed by the direct action of acetylene upon aqueous or ammoniacal solutions of cuprous and silver salts.[1] Mercury and gold compounds have also been obtained, and it seems probable that these are of analogous composition.

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[1] Acetylene passed into a concentrated aqueous solution of silver nitrate gives a white precipitate which is much more explosive than the compound prepared from an ammoniacal solution. It has the composition represented by the formula $C_2Ag_2.AgNO_3$.

	Calculated for $C_2Ag_2.AgNO_3$.	Found.
Ag	79.02	79.06

With dilute aqueous solution of silver nitrate C_2Ag_2 is formed. With ammoniacal silver chloride solution C_2Ag_2 is precipitated.

When finely divided metallic copper, obtained by precipitation, is suspended in water and acetylene passed through, the copper is partially converted into C_2Cu_2.

MENTHENE.

By F. A. Sieker and Edward Kremers.

In a recent number of the "Berichte"[1] Brühl states that menthene can be obtained by the dehydration of menthol with anhydrous copper sulphate. A year ago one of us[2] reported on some oximes obtained from pennyroyal oil, and mentioned incidentally that dehydration experiments with menthone were being conducted. The investigation had to be interrupted, and since the anticipations were not realised, the dehydration of menthol was taken up in preference. This has been effected in various ways since Walter in 1838 first prepared menthene by the action of glacial phosphoric acid upon menthol. The dehydrating agents, phosphoric acid anhydride, zinc chloride, sulphuric acid, etc., however, not only effect the hydration of menthol, but also destroy in part the desired hydrocarbon, as becomes quite evident from the large percentage of by-products resulting. Since potassium acid sulphate has been of such admirable service in the dehydration of terpineol and terpin, it was tried and soon proved to be very satisfactory. After this fact had been established and while we were trying to make the nitrosite and nitrosyl-chloride addition-products of the hydrocarbon, Brühl's report came to our notice. We, therefore, feel constrained to make this preliminary report.

To prepare menthene, 50 grams of menthol and 100 grams of potassium acid sulphate are heated in a strong flask connected with a reflux condenser on a paraffin-bath for 6–8 hours at a temperature of from 180°–200°. The mixture is then distilled with water-vapor and the oily distillate is dried with the aid of caustic potassa. After repeated careful fractionation the oil was resolved chiefly into menthene, boiling at 167°–168°, and unchanged menthol. The by-products are altogether insignificant. The menthene thus obtained is a colorless, mobile liquid of a peculiar (*not menthol-like*) odor. Its specific gravity at 20° was found to be 0.814. It is strongly *dextro-gyratory*, whereas the menthol from which it is obtained is laevo-gyratory: $[\alpha]_D = +26\ 40°$.[3]

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[1] "Untersuchungen über die Terpene und deren Abkömmlinge," Ber. d. chem. Ges. **25**, 142.

[2] Pharm. Rundschau, 1891, p. 131.

[3] The higher fractions have a somewhat higher specific gravity, but are optically less active, thus indicating the presence of unchanged menthol. More careful determinations of the physical constants have been recently made by Mr. Urban.

Upon combustion it yielded the following results:

0.1664 gram substance gave 0.5250 gram CO_2 = 0.14318 gram C; and 0.1966 gram H_2O = 0.02184 gram H.

	Calculated for $C_{10}H_{18}$.	Found.
C	86.95	86.04
H	13.04	13.12

As already mentioned, the investigations of menthene heretofore were more or less unsatisfactory because no crystalline derivatives were obtained. Since the nitrosites, nitrosates and nitroso-chlorides of the terpenes were found to be of such value in the isolation and investigation of the terpenes, the attempt was made to prepare one of these compounds from menthene. The nitrosite reaction as applied to terpinene by Wallach was not successful. The nitroso-chloride reaction, however, proved to be a success. 15 cc. of menthene were dissolved in 15 cc. of glacial acetic acid and 11 cc. of ethyl nitrite, and the solution kept cold in a freezing-mixture. To it 6 cc. of hydrochloric acid, previously dissolved in an equal volume of glacial acetic acid, were added gradually. A white crystalline precipitate was formed, and was separated by filtration and dried on porous plate. 15 grams of menthene yielded about 4 grams of nitroso-chloride. The nitroso-chloride was purified by dissolving it in the smallest possible quantity of chloroform, filtering the solution and precipitating with alcohol.

The nitroso-chloride thus purified is a white crystalline powder, that showed no signs of decomposition even after three weeks. It melts at 113° *without decomposition*, but decomposes, as shown by the evolution of gases, at about 152°. It is altogether remarkable for its stability. Even in contact with the acid mother-liquid it shows no signs of decomposition after several days when kept cold. It is readily soluble in chloroform, not quite as soluble in ether, and but sparingly soluble in alcohol.

Upon analysis it yielded the following results:

I. 0.1920 gram substance gave 0.4101 gram CO_2 = 0.11184 gram C; and 0.1589 gram H_2O = 0.01765 gram H.

II. 0.1998 gram substance gave 12 cc. N at 17° under pressure of 746 mm. = 0.0136737 gram N.

III. 0.2004 gram substance gave 0.1305 gram AgCl = 0.03227 gram Cl.

Calculated for $C_{10}H_{18}NOCl$.		Found.		
		I.	II.	III.
C	58.99	58.24	...	...
H	8.84	9.19	...	...
N	6.88	...	6.84	...
Cl	17.40	...	...	16.10

By heating menthene nitroso-chloride with an alcoholic solution of benzyl-amine a crystalline substance was obtained which very likely is a nitrol-amine base.

Menthene being a derivative of tetrahydro-benzene, its first crystallisable derivative must be of considerable interest, especially as this must, no doubt, lead to many more. A study of these derivatives must also throw more light upon the analogous derivatives of the terpenes. The disputed question whether menthene occurs in oil of peppermint or not can now be answered; the identity of dihydro-dipentene ("Dihydrocynen") with menthene also can be established or denied. By splitting off hydrogen chloride from the nitroso-chloride, dihydro-carvoximes may be expected to result, etc., etc. The study of menthene, of its nitroso-chloride and other derivatives, will be continued.

PHARMACEUTICAL LABORATORY, UNIVERSITY OF WISCONSIN, *April* 20, 1892.

Contributions from the Chemical Laboratory of Wesleyan University.

X.—ON THE ACTION OF ACETYL CHLORIDE ON ORTHO-HYDROXY-ALDEHYDES.

BY W. P. BRADLEY AND F. B. DAINS.

Nearly three years ago an advance paper was published by one of the writers[1] describing the first results of an investigation of disalicylic aldehyde. The present paper is in continuation of the same work, which was for some time unavoidably interrupted.

Disalicylic aldehyde, $C_{14}H_{10}O_3$, was first obtained by Ettling[2] as a product of the dry distillation of the copper salt of salicylic aldehyde. In 1851 Cahours[3] obtained it, strangely enough, by the action of benzoyl chloride on salicylic aldehyde. Later investigations[1] have shown that acid chlorides in general convert free salicylic aldehyde into this condensation-product. The effect of their action is therefore the extraction of one molecule of water from two molecules of the aldehyde, which may be represented by the formula:

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[1] Ber. d. chem. Ges. **22**, 1134. See also W. P. Bradley: Inaug. Diss., Göttingen, 1890.

[2] Ann. Chem. (Liebig) **35**, 255; **53**, 77.

[3] Ibid. **78**, 228.

$$2C_7H_6O_2 = C_{14}H_{10}O_3 + H_2O.$$

So far as is known, no other dehydrating agents produce this compound.

Disalicylic aldehyde possesses none of the properties of aldehydes or phenols. Ordinary oxidising agents do not affect it, nor can it be reduced. It unites neither with phenyl-hydrazine nor with hydroxyl-amine. It is insoluble in alkalies and is not affected even by melted potassium hydrate. Certain acid reagents, however, reconvert it into salicylic aldehyde or derivatives of it. Thus, a quantitative yield of salicylic aldehyde is obtained by the action of concentrated sulphuric acid at the ordinary temperature. Fuming hydrochloric acid at 120°–130° produces the same result, but incompletely. Bromine dissolved in glacial acetic acid yields a mixture of monobrom and dibrom-salicylic aldehyde, para-dibrom-disalicylic aldehyde, $C_{14}H_8Br_2O_3$, and considerable quantities of unchanged disalicylic aldehyde. Nitric acid of sp. gr. 1.44, when boiled with powdered disalicylic aldehyde, produces a dinitro-salicylic acid.

Until the present portion of the work of investigating disalicylic aldehyde was commenced, but a single derivative of the compound was known, viz. the dibrom-derivative mentioned above. From the mixed product resulting from the action of bromine upon disalicylic aldehyde, the monobrom and dibrom-salicylic aldehydes, being soluble in alkali, were easily removed; but all attempts to separate the unchanged disalicylic aldehyde completely from its dibrom-derivative failed. Although a pure compound could not be obtained in this way, it was found that the same method used to produce disalicylic aldehyde from salicylic aldehyde could be employed to convert monobrom-salicylic aldehyde into dibrom-disalicylic aldehyde. The large yield obtained could easily be separated from any unchanged brom-salicylic aldehyde by the use of alkali, in which of course the latter is soluble. It seemed, therefore, probable that this peculiar reaction of acetyl chloride might prove to be of general application to all aldehydes having an hydroxyl group in the ortho position. With the object in view of testing the truth of this conclusion, the following ortho-hydroxy-aldehydes have thus far been studied.

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[1] Ann. Chem. (Liebig) **145**, 299; Suppl. **8**, 42; **244**, 46.

Para-chlor-salicylic aldehyde.—Para-chlor-salicylic aldehyde[1] (m. p. 99.5°) was prepared by leading a stream of dry chlorine gas into salicylic aldehyde dissolved in glacial acetic acid. The solution turns yellow, becomes warm, and if not too dilute, deposits crystals of chlor-salicylic aldehyde. A small amount of dichlor-salicylic aldehyde forms at the same time. In order to bring about condensation, the former was subjected in the main to the same treatment which had been found successful in the case of the analogous monobrom-salicylic aldehyde. A small excess of glacial acetic acid was employed as a solvent, and an amount of acetyl chloride was added equal in weight to half the chlor-salicylic aldehyde employed. Reaction begins at once with evolution of considerable heat. After standing several hours the mixture is heated on the water-bath to complete the reaction, and then poured into water. Dichlor-disalicylic aldehyde together with some unchanged monochlor-salicylic aldehyde is precipitated in solid form, and may be obtained free from the latter by washing with dilute alkali. It will be well to state that as a rule it is not advisable to increase the relative amount of acetyl chloride employed beyond what is indicated above. In some cases, notably that of para-methyl-salicylic aldehyde, to be described later, such an increase leads to the formation of large quantities of a gummy substance, difficult or impossible to work.

The yield of dichlor-disalicylic aldehyde averages about 60–70 per cent. of the theoretical. This compound does not crystallise notably well from any solvent yet tried. From a hot concentrated solution in alcohol it may be obtained in fine white silky needles. Out of more dilute solutions it crystallises in very long slender filaments, which fill the entire liquid as with a kind of moss or mould. In either case the crystals melt at 172°.

Analysis.—0.1902 gram compound gave 0.1874 gram AgCl (Carius).

	Found.	Calculated for $C_{14}H_8Cl_2O_3$.
Cl	24.27	24.03

Dichlor-disalicylic aldehyde is quite easily soluble in alcohol, ether, acetic acid, benzene, chloroform, and carbon bisulphide, less soluble in petroleum ether. Like disalicylic aldehyde itself, it is easily soluble in concentrated sulphuric acid, and the resulting amber-colored liquid, when poured into water, deposits quantitatively para-chlor-salicylic aldehyde.

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[1] Ann. Chem. (Liebig) **30**, 171; Berzelius' Jsb. **20**, 311.

Dibrom-dichlor-salicylic aldehyde.—Dibrom-salicylic aldehyde[1] (m. p. 82.5°), whether treated with acetyl chloride in the usual way, or in a sealed tube at 115°–130° C., gave no traces of any condensation-product, but was recovered unchanged. Similarly with dichlor-salicylic aldehyde no condensation could be effected, as far as our experiments with it extended.

Para-nitro-salicylic aldehyde.—Para-nitro-salicylic aldehyde[2] was dissolved in glacial acetic acid and half its weight of acetyl chloride was added. There was no rise of temperature, and no condensation took place. In subjecting the mixture, however, to a temperature of a 100° C. in a sealed tube, a very small quantity of a substance was obtained which was insoluble in alkali, and which was deposited from its solution in ether in small yellow crystals melting at about 220° C. All efforts to secure in this manner enough of the substance to purify and analyse proved fruitless, and yet, in view of what follows, it can hardly be questioned that we were dealing with para-dinitro-disalicylic aldehyde. We were in fact able to obtain the latter by a direct nitrification of disalicylic aldehyde itself; for while boiling nitric acid of 75 per cent.[3] by cleavage, oxidation, and nitrification produces at once nitro-derivatives of salicylic acid, it was discovered that fuming acid at 0° C. effected simply the introduction of nitro groups into the molecule of disalicylic aldehyde.

Into successive portions of fuming nitric acid of about 20–25 cc. each, well cooled in ice-water, finely powdered disalicylic aldehyde was dropped in small quantities and agitated as long as it dissolved easily. All rise of temperature must be carefully avoided, in order to prevent the formation of considerable quantities of a glue-like substance which seriously interferes with the subsequent crystallisation and purification of the nitro-products formed. When the operation is ended the red liquid is allowed to remain about fifteen minutes at 0° and is then poured into a large quantity of ice-water. The solid precipitate which forms is washed thoroughly with dilute alkali and with water. It is composed mainly of para-dinitro-disalicylic aldehyde, with a probable admixture of mononitro and trinitro compounds,—possibly, also, of isomeric dinitro-derivatives. Great difficulty was encountered in the separation of the individual components. After a long and wearisome process of fractional crystallisation out of acetic acid and benzene,—these solvents having been found to give most satisfactory results—the greater portion of the yield was obtained in the form of small, compact, strongly refracting crystals, of a pale yellow color, and melting at 221° when pure.

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[1] Ann. der Phys. Pogg. **46**, 71; Berzelius' Jsb. **25**, 486; Bull. Soc. chim. (Paris) **46**, 277; and Inaug. Diss., p. 30.

[2] Ber. d. chem. Ges. **20**, 1928.

[3] Inaug. Diss., 29.

Analysis.—I. 0.4239 gram substance gave 0.1025 gram H_2O and 0.8254 gram CO_2.

II. 0.2614 gram substance gave 20.2 cc. N measured at 759 mm. of mercury and 11.5° C.

	I.	II.	Calculated for $C_{14}H_8(NO_2)_2O_3$.
C	53.10	...	53.17
H	2.68	...	2.53
N	...	9.18	8.86

Para-dinitro-disalicylic aldehyde dissolves with difficulty in alcohol, acetic acid, ether, chloroform, carbon bisulphide, and petroleum ether, and but little more freely in benzene. The striking similarity in every respect between this compound and that obtained from para-nitro-salicylic aldehyde by means of acetyl chloride, left little doubt as regards the position of the nitro groups in it. Direct proof was furnished by the action of concentrated sulphuric acid upon the compound. Solution was easily effected with the aid of gentle heat, and the addition of water to the red liquid precipitated quantitatively para-nitro-salicylic aldehyde, melting at 126°.

Out of the same mixture of nitro-products from which para-dinitro-disalicylic aldehyde was isolated, at least two other fractions were obtained, which showed fairly constant melting-points of about 180° and 250° respectively. The conclusion was easy that these contained respectively a mononitro and a trinitro-derivative of disalicylic aldehyde; but as neither of the fractions could be obtained in quantities large enough to admit of the necessary purification, no proof of its correctness could be furnished.

Ortho-nitro-salicylic aldehyde.[1]—Ortho-nitro-salicylic aldehyde (m. p. 109°) appears to be wholly unaffected by acetyl chloride, both at ordinary temperatures and in a sealed tube. No condensation-product was obtained in this way, nor could any ortho-dinitro-disalicylic aldehyde be obtained by the direct nitrification of disalicylic aldehyde.

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[1] Ber. d. chem. Ges. **20**, 1928.

α-Aldehydo-β-naphthol.[1]—This compound, obtained by Kauffmann by the action of chloroform and potassium hydroxide upon β-naphthol, condenses very easily indeed by the use of acetyl chloride. The reaction is accompanied by evolution of heat and the deposition of a part of the condensation-product sought in crystalline form. The total yield is nearly quantitative. For purposes of purification, acetic acid or benzene may be employed as solvents. After one or two crystallisations, the product, β-diortho-oxy-α-naphthaldehyde, is found to be sufficiently pure for analysis.

Analysis.—I. 0.3386 gram substance gave 0.1324 gram H_2O and 1.0018 grams CO_2.

II. 0.3358 gram substance gave 0.1294 gram H_2O and 0.9928 gram CO_2.

III. 0.3102 gram substance gave 0.1199 gram H_2O and 0.9154 gram CO_2.

	Found.			Calculated for
	I.	II.	III.	$C_{22}H_{14}O_3$.
C	80.56	80.65	80.48	80.98
H	4.19	4.29	4.29	4.30

The compound dissolves with difficulty in the ordinary solvents. From benzene or acetic acid it is deposited in small, hard, nearly white crystals, melting at 241° C., which soon acquire a tinge of red. Concentrated sulphuric acid dissolves it, as it does all the condensation-products of this class so far investigated. The solution is of a dark-red color, with a green fluorescence, and when diluted with water deposits α-aldehydo-β-naphthol.

Para-methyl-salicylic aldehyde.[2]—The method here employed with ortho-oxy-aldehydes gave with para-methyl-salicylic aldehyde a nearly quantitative yield of para-dimethyl-disalicylic aldehyde. After washing the latter thoroughly with dilute alkali it was found to contain traces of chlorine when heated upon a piece of copper oxide in the colorless Bunsen flame. After repeated crystallisations the halogen still remained. It was found advisable, therefore, to boil the crude condensation-product with a concentrated solution of alkali for 15–20 minutes, after which it showed no trace of halogen and was easily purified by recrystallisation. In a state of purity it melts at 141° C.

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[1] Ber. d. chem. Ges. **15**, 805.

[2] Ibid. **11**, 773.

Analysis.—0.2172 gram substance gave 0.1086 gram H_2O and 0.5997 gram CO_2.

	Found.	Calculated for $C_{16}H_{14}O_3$.
C	75.30	75.60
H	5.51	5.56

Although para-dimethyl-disalicylic aldehyde is not readily soluble in acetic acid, it is sufficiently so to allow of a determination of its molecular weight by the method of Raoult. 74.25 grams of glacial acetic acid were used as a solvent. A depression in the freezing point amounting to 0.046° was obtained by the solution of 0.1797 gram of the substance under discussion. This corresponds to a molecular weight of 251.2. The calculated value is 254.

The compound is quite easily soluble in most solvents. Petroleum ether dissolves it with difficulty and deposits it in beautiful oblong tables pointed at either end. Para-dimethyl-disalicylic aldehyde differs from the derivatives thus far mentioned in being easily volatile with steam, although considerably less so than disalicylic aldehyde itself. Concentrated sulphuric acid reconverts it into para-methyl-salicylic aldehyde.

Efforts to oxidise one or both methyl groups to carboxyl have thus far failed. Protracted boiling with even a 15-per cent. alkaline solution of permanganate produced no effect.

Ortho-aldehydo-salicylic acid.—This compound, prepared according to directions given by Reimer and Tiemann,[1] is not condensed in the slightest degree by acetyl chloride, even when a mixture of the two is heated in a sealed tube to 150° C.

The ultimate object of the general investigation of which the above is a part, is the determination of the constitution of disalicylic aldehyde, for which a provisional formula has already[2] been proposed. Work along these and cognate lines will be continued. Among the compounds whose conduct is to be studied are aldehydo-derivatives of ortho- and meta-kresol, of resorcin and pyrocatechin or their ethers; ortho-hydroxy-ketones; and hydroxy-aldehydes and ketones of the methane series. As regards the special question whose answer was sought in the foregoing experiments, it is obviously too early as yet to draw definite conclusions. It appears probable, however, that acetyl chloride is able to secure quantitative condensation of all ortho-hydroxy-aldehydes in which only hydrocarbon groups are joined directly to the benzene ring. The introduction of negative groups hinders or entirely prevents condensation. Thus the presence in the molecule of a single chlorine or bromine atom diminishes the yield 30–40 per cent. The presence of a single nitro group in the para position nearly prevents condensation. A nitro group or a carboxyl in the ortho position, or the presence of two halogen atoms, prevents it altogether.

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[1] Ber. d. chem. Ges. **9**, 1272; **10**, 1564.

[2] Inaug. Diss., p. 37.

A NEW COLOR-STANDARD FOR NATURAL WATERS.

By Allen Hazen.

After the disease-producing qualities, which we may believe are mainly dependent upon living germs, there is no subject connected with the examination of potable waters which deserves more careful consideration than their physical characteristics. The public very properly desire that the water which they drink shall not only be of such purity that it will not cause diarrhea, typhoid fever or other disease, but also that it shall be free from offensive tastes, odors and appearance. It is well known that these physical characteristics bear no definite relation to the power of causing serious disease; that dirty and discolored waters may nevertheless be not unwholesome, while in some cases a beautifully clear water may carry the germs of typhoid fever; and it is not with any intention of determining the wholesomeness of waters that we undertake the study of their colors. We wish to know how various water supplies compare in color; what changes take place in the same supply at different seasons of the year, and what treatments and conditions remove or tend to remove color. In order to obtain this information we require a standard by which to measure accurately the colors in question,—a standard which shall be the same at all times in the same laboratory, and that can be conveniently prepared by different chemists so as to yield strictly comparable results.

Standards now in Use.

As early as 1878[1] Prof. A. R. Leeds suggested the use of nesslerised ammonia as a standard of color. The color of a water was recorded as the number of cc. of an ammonia solution, 0.01 mg. NH_3 per cc., which when mixed with 50 cc. of distilled water and nesslerised would produce an equal color. The great advantages of this process were the ease and simplicity of the determination, as the necessary apparatus and standards were always present in laboratories for water analysis, being required for another purpose; and also that the figures were supposed to have a definite value based on the amount of ammonia used. The objections to its use, as will be shown, are that the colors depend upon temperature, and upon the composition and amount of the Nessler reagent used, and upon other details of manipulation to such an extent as to make uncertain the exact value of the results, and also that the figures obtained are not proportional to the coloring matter present.

The use of highly colored natural waters for standards, the colors of which are checked by comparison with nesslerised ammonia, and which are diluted for use as required, as suggested by Mrs. Richards,[2] overcomes some of the objections to the nesslerised ammonia standard, but at the same time makes the process somewhat arbitrary.

In 1881 Messrs. Crookes, Odling and Tidy[3] described an instrument for measuring the colors of waters. It consisted of a pair of 2-ft. tubes, one of which contained the water under examination, while the other remained empty. Behind the empty tube were placed two hollow wedges, one containing a 1-per cent. copper sulphate solution, the other a solution of ferric and cobalt chlorides containing 0.7 gram iron and 0.3 gram cobalt per liter, with "a very slight excess of free hydrochloric acid." These wedges were pushed over the empty tube until their color matched that of the water in the other tube, and the color was recorded as equal to so many millimeters of blue and of brown solutions. With this apparatus the colors of the various water-supplies of London have been measured up to the present time. The fatal objection to this process is that the color of the brown solution is affected by the amount of free hydrochloric acid, and by temperature, to such an extent that it is totally unfit for a general standard.

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[1] Proc. Am. Chem. Soc. **2**.

[2] Rep. Mass. State Board of Health, Examination of Water Supplies, 1890, p. 532.

[3] Chem. News. **43**, 174.

Platinum Color-Standard.

The objections to the nesslerised ammonia standard may be avoided in another way, while still retaining its simplicity, by the use of colored metallic solutions of definite composition. The use of iron for this purpose is inadmissible, as has been said, because its color depends in a controlling degree upon acidity and temperature, but the colors of several other metallic salts are quite independent of these conditions, and may therefore be used. A mixture of the chlorides of platinum and cobalt leaves little to be desired. The color of such a solution is, within wide limits at least, entirely independent of acidity and temperature, and when mixed with a moderate amount of hydrochloric acid, it is quite stable even in direct sunlight.

By varying the ratio of cobalt to platinum, the hue of any clear natural water, when not seen in too great depth, can be perfectly matched; but for all practical purposes, a single solution containing one-half as much cobalt as platinum is sufficient. Some waters will appear slightly redder than this; some slightly greener; but the differences are very much less than those between waters and nesslerised ammonia, and are quite unimportant.

We can conveniently express the color of a water in terms of the amount of platinum required to produce an equal color, and we have: *The color of a water is the amount of platinum, in parts per ten thousand, which, in acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water.* I suggest that this be called the *platinum color-standard.*

Method of Application.—To make the standards, a solution having a color of 5. is a convenient starting-point. This can be made by dissolving 1.246 grams potassium-platinum chloride, containing 0.5 gram platinum, and 1 gram crystallised cobalt chloride, free from iron, containing 0.25 gram cobalt, in water with 100 cc. concentrated hydrochloric acid, and making up to one liter. A solution so prepared has remained unaltered for one year, although exposed to the light, and at times to direct sunlight. Standards for use are made by diluting 1, 2, 3 cc. etc., of this solution to 50 cc. in Nessler tubes, giving colors 0.1, 0.2, 0.3, etc. In clean tubes, and protected from dust when not in use, they will keep for months, and can be replaced at any time from the strong solution.

If the standards made as above do not perfectly match waters having hues different from those with which we are familiar, more or less cobalt may be used, keeping the platinum, which is the real standard, always the same.

Long Tubes for Low Colors.—Colors can be read as described above in 200-mm. Nessler tubes with ample accuracy for all ordinary purposes; but for some experimental work with clear light-colored waters, where the greatest possible accuracy was desired, 600-mm. tubes have been found more satisfactory. We have used a pair of brass tubes closed with plate-glass ends, from which the luster of the brass inside was removed by a dilute solution of sugar of lead. One tube is filled with distilled water, the other with the water under examination. The tubes, held by a suitable support, are pointed at a piece of ground glass in a window, with a slight angle between themselves so that the contents of both tubes can be seen from a little distance with one eye. If the two tubes look alike, the water is colorless; that is, it contains no foreign coloring matter. If the water is yellow, it is matched by placing a flat-sided jar of platinum cobalt solution behind the distilled water. The jars, of which there are a series corresponding to colors 0.01, 0.02, 0.03, etc., contain standard solutions as many times as strong as would be used for direct comparison, as the 600-mm. tube of water is longer than the thickness of the solutions in the jars.

The results so obtained are directly comparable with readings in Nessler tubes in the case of clear waters with colors of 0.3 or less, and the probable error is very much less. With turbid waters, however, the results in the long tubes are higher, the difference increasing with the turbidity.

Instead of using a single set of jars, each containing both platinum and cobalt, two sets can be used—one of platinum and one of cobalt. In this way the hues of different waters, and particularly those of turbid waters, can be more accurately matched, and also, if desired, a record can be made in each case of the ratio of cobalt to platinum required. This method is considerably more laborious than when the two metals are combined in a single solution, and the results obtained very rarely differ to an appreciable extent.

Limit to the Length of Tube.—The 600-mm. tubes should not be used for water having more than a very slight turbidity, or for colors above 0.3, as in such cases a more accurate comparison can be made in a less depth of liquid. In the same way, with very highly colored waters, the best results are obtained with columns of liquid shorter even than a 200-mm. Nessler tube, and, in a general way, it may be said that the product of the color and the depth of water used for comparison in millimeters should not exceed 180. Thus colors above 0.3 should not be read in 600-mm. tubes; above 0.9, in 200-mm. tubes; above 1.8, in 100-mm. tubes, etc. This is particularly important when only a single ratio of cobalt to platinum is used; for with the same water in great depth, more cobalt is required in proportion to the platinum than in a less depth. Up to the limit given these variations are quite unimportant, and do not in any way affect the results; but with deeper colors the variations increase far more rapidly than the increase in color, and may seriously vitiate the results if tubes are used considerably longer than the above limits. Instead of using very short tubes for extremely high colors, good results can be obtained by diluting the water five or ten times with distilled water, and calculating the original color from the measured color of the dilution.

The Nesslerised-Ammonia Standard.

We have at the present time the records of many thousand water analyses in which the colors have been determined by comparison with the nesslerised-ammonia standards. In fact, it might almost be said that all our knowledge of the colors of American waters is expressed in terms of this unit. It is, therefore, of prime importance to inquire how the proposed standard compares with that most generally in use.

Some Considerations in regard to Nesslerisation.—The colors produced by nesslerising ammonia depend upon temperature, and upon the quality and quantity of Nessler reagent, and upon whether the ammonia is mixed with the water before nesslerisation or not. The Nessler solution used for the following experiments, except when otherwise stated, was made by dissolving 70 grams potassium iodide in a little water, adding cold saturated solution of mercuric chloride to slight permanent pink, then 500 cc. of a solution of potassium hydrate (500 grams per liter), and 10 cc. more mercuric chloride. Water is added to make 2 liters, and it is allowed to stand some days before use. The ammonia-free water used for making the standards was prepared by blowing steam through ordinary good distilled water, and contained, as found by distillation, 0.0002 to 0.0004 part per 100,000 ammonia. The standard ammonia solution, containing 0.01 mg. ammonia per cc., was thoroughly mixed with this water before nesslerising with 2 cc. of reagent, at temperatures ranging only from 18° to 21°. The colors produced at the end of half an hour were measured by the platinum color standard as described above, except that no cobalt was required to match the lower Nessler standards, as they have much less red than natural waters.

Quantity of Nessler Reagent used.—The following table shows the colors produced by nesslerising different amounts of ammonia with 0.5, 1, 1.5, 2, 2.5, and 4 cc. of Nessler reagent:

Nessler reagent used,		0.5	1.0	1.5	2.0	2.5	4.0
Ammonia solution,	0	.05	.07	.10	.14	.17	.25
	0.1 cc.	.05	.07	.10	.16	.22	.37
	0.2	.05	.07	.18	.30	.37	.45
	0.3	.05	.15	.37	.43	.45	.55
	0.5	.13	.45	.55	.60	.62	.65
	1.0	.65	.90	1.00	1.05	1.10	1.15
	2.0	1.30	1.80	1.90	2.00	2.00	2.00
	4.0	3.80	4.50	5.00	5.00	5.00	5.00

With the lower standards the colors depend quite as much upon the quantity of Nessler reagent as upon the quantity of ammonia. Thus the 0.2 standard with 1.5 cc. reagent, the 0.1 standard with 2 cc., and distilled water with 2.5 cc. give substantially equal colors. With the higher standards the quantity of reagent is of less consequence. An interesting point is that a certain amount of reagent is required to produce any color with the low standards; 0.5 cc. reagent produces no color whatever, that is, no more than its own color in distilled water, when added to the 0.3 standard; 1 cc. reagent does not bring out the 0.2 standard; and 2 cc., the usual quantity, hardly affects the 0.1 standard, 2.5 cc. being required to show a distinct increase in color.

When a set of standards is made from water absolutely free from ammonia and with the usual Nessler reagent, there will be hardly any color in the 0.1 standard above that of the nesslerised distilled water; the higher standards will increase regularly in color. If, however, instead of strictly ammonia-free water, a water containing 0.0010 or 0.0020 ammonia is used, and such a water would be considered "ammonia-free" if not tested by distillation, the blank shows only the color of the Nessler reagent, while the 0.1 and succeeding standards show a regular and marked increase in depth. Such a set of standards is apparently more satisfactory than those made from strictly ammonia-free water, but will obviously give quite different color results. The 0.1 standard can be brought out by using either more or stronger Nessler reagent; but if this is done, all the colors will differ from those obtained under the usual conditions.

Quality of Nessler Reagent.—Different samples of Nessler reagent differ considerably in the colors which they produce with the lower standards, even when made by the same formula.

Other conditions being the same, the amount of color produced with the lower standards increases with the alkali in the reagent used. Three lots of Nessler solution were made side by side and in precisely the same way, except that the amount of caustic potash was varied, the three portions containing 50, 125, and 200 grams per liter respectively. The colors produced by nesslerising ammonia with 2 cc. of these solutions were as follows:

Quantity of alkali in Nessler reagent:

Ammonia Solution.	50 grams KOH.	125 grams KOH.	200 grams KOH.
0	.22	.14	.15
0.1 cc.	.22	.16	.20
0.2	.25	.37	.40
0.3	.30	.45	.50
0.5	.40	.62	.65
1.0	.90	1.05	1.05

The colors also depend upon the amount of potassium iodide and mercuric chloride present. Three lots of Nessler solution were prepared containing respectively 20, 35, and 50 grams potassium iodide per liter, with corresponding amounts of mercuric chloride, the alkali being 125 grams in each case. The colors produced were as follows:

Quantity of iodide in Nessler reagent:

Ammonia Solution.	20 grams KI.	35 grams KI.	50 grams KI.
0	.13	.14	.25
0.1 cc.	.13	.16	.37
0.2	.13	.37	.50
0.3	.30	.45	.58
0.5	.55	.62	.70
1.0	1.05	1.05	1.10

When both alkali and iodide vary, the result is the same as with varying amounts of the same solution; 2 cc. of a dilute reagent give the same result as 1 cc. of twice as concentrated a solution.

Mixing.—With the standards 0.1 and 0.2 a much higher color than is otherwise obtained is produced when the ammonia is added to the distilled water in the tube and is immediately nesslerised before it becomes mixed with the water. With the standards 0.3 and above, no corresponding differences are observed. The average results obtained are as follows:

Effect of mixing:

Ammonia Solution.	Mixed.	Not Mixed.
0	.14	.14
0.1 cc.	.16	.26
0.2	.30	.37
0.3	.43	.45
0.4	.52	.52

Temperature.—The color produced by nesslerising ammonia also depends upon temperature;[1] the higher the temperature the darker and redder is the color produced, but with the lower standards the errors introduced by variations of not more than two or three degrees are comparatively small.

Bearing upon Ammonia Determinations.—It will be observed that the above-mentioned sources of error in the measurement of colors have no direct bearing upon the accuracy of ammonia determinations when properly carried out. There, the absolute amount of color is of no consequence; it is only important that under the same conditions equal quantities of ammonia yield equal colors. The results suggest, however, the necessity of accurately measuring the Nessler reagent used, especially for the lower standards, and of having strictly ammonia-free water and a sufficiently concentrated and sensitive Nessler reagent to strike colors with the lowest standards.

Comparison of the Platinum and Nesslerised-ammonia Standards.

It can hardly be expected, in view of the above observations, that the same results will be obtained with the nesslerised-ammonia standard in different laboratories. It would seem inevitable, in the absence of a rigorous definition of the details of manipulation, that different workers should obtain different results. In giving the following figures, which are the average of a large number of trials made under the conditions indicated above, I am fully aware that they represent the nesslerised-ammonia standard only as it has been used in this laboratory, and that great caution must be used in applying them to results obtained by that process elsewhere.

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[1] This Journal **12**, 425.

Nesslerised Ammonia.	Platinum.	Nesslerised Ammonia.	Platinum.
0	0.14	0.7	0.78
0.1	0.16	0.8	0.87
0.2	0.30	0.9	0.96
0.3	0.43	1.0	1.05
0.4	0.52	1.5	1.50
0.5	0.60	2.0	2.00
0.6	0.69	3.0	2.80

These figures bring out some interesting facts. The nesslerised-ammonia standard has no place for colors which match less than 0.14 platinum. All that can be done with waters having colors below 0.1 and yet having definite colors, is to record them as 0.05—an arbitrary proceeding, since the color is by no means equal to that obtained by nesslerising 0.05 cc. ammonia solution in 50 cc. distilled water. With the nesslerised-ammonia standard the figures obtained are not proportional to the color: color 0.5 is only twice as deep as color 0.2; color 0.8 is only twice as deep as color 0.3; color 1.0 is only twice as deep as color 0.4, etc. The following figures showing the colors of dilutions of a highly colored water as read against the two standards show that these are real and not merely apparent differences.

Dilution of a highly colored water:

Dilution. Per cent. of Colored Water.	Calculated. Color.	Colors as Measured.		
		Nesslerised Ammonia.	Platinum.	
			Nessler Tube.	600-mm. Tube.
100	2.10	2.30	(2.30[1])	...
50	1.05	1.00	(1.10[1])	...
33⅓	.70	.60	.70	...
25	.52	.40	.53	...
20	.42	.30	.43	...
10	.21	.10	.22	.20
4	.08	0	.08	.08

[1] Above the limit of color for 200-mm. tubes; the hues in these cases do not perfectly match and the results are only approximate. In practice these colors are calculated from the more accurate readings of one of the lower dilutions, or else a depth of less than 200 mm. should be used for the comparison.

It will be seen that the colors as measured by the platinum standard (calculating those above the limits of color for the depth of liquid), are strictly proportional to the quantity of coloring matter in the various dilutions, while with the nesslerised ammonia the figures differ materially from the calculations, always indicating a greater reduction in color than corresponds to the extent of dilution. Moreover, if more Nessler reagent, or a more sensitive reagent, had been employed, or if the distilled water used had contained a trace of ammonia, even though too little to be shown by direct nesslerisation, the lower figures would have been farther reduced, and still greater deviations from the calculated colors would have resulted.

Taking into account the unavoidable variations due to the imperfections of the nesslerised-ammonia standard, the two standards agree strikingly, and it would hardly be possible to secure a standard free from the defects of the nesslerised ammonia which would at the same time better agree with it at all points. This is a most important point in connection with the extensive records of color already obtained with the use of the older standard.

Conclusions.

The nesslerised-ammonia standard of color, although the best heretofore proposed, is open to very serious objection owing to the great range in the standard colors with comparatively slight variations in manipulation, the colors of the lower standards depending quite as much upon the quantity and quality of Nessler reagent employed as upon the ammonia; and also to the fact that the numbers expressing the colors are not directly proportional to the colors themselves. It also fails to provide a place for the large number of waters having colors less than that of nesslerised distilled water.

In the *platinum color-standard* now proposed the above imperfections are entirely overcome. The necessary standards are easily prepared of exact strength, and are unimpeachable in the constancy and permanency of their colors, which are not affected by any reasonable variation in the manipulation employed. The hue of the standards can be made to match that of natural waters allowing more accurate comparisons than are possible with nesslerised ammonia, and, within reasonable limits, the figures obtained are directly proportional to the actual colors.

The figures obtained are approximately equal to those of the nesslerised-ammonia standard, differing only so much as is necessitated by the imperfections of the latter, so that the adoption of the platinum standard will make the minimum disturbance with the data already accumulated.

In conclusion, I wish to acknowledge my obligation to Prof. T. M. Drown, of the Massachusetts Institute of Technology, for many valuable suggestions, and also to Mr. H. W. Clark for the assistance he has given in these investigations.

LAWRENCE EXPERIMENT STATION, MASSACHUSETTS STATE BOARD OF HEALTH.

THE CONDENSATION-PRODUCTS OF FURFUROL WITH AROMATIC BASES.

BY G. J. L. DE CHALMOT.

Furfurol, aniline and aniline hydrochloride when mixed together, whether in solution or not, react upon one another with the formation of a violet-red crystalline compound. Stenhouse[1] was the first to examine this product with care. He showed that it was formed by the direct combination of one molecule each of furfurol, aniline and aniline hydrochloride, and that the composition of the compound could be represented by the formula $2C_6H_7N.C_5H_4O_2.HCl$, there being no splitting off of water. A similar compound is formed if toluidine be substituted for aniline. From these dyestuffs he was able by means of ammonia to prepare basic substances, but only in the form of impure, yellowish brown, gummy products which could be preserved only when protected from the light and kept in a vacuum over sulphuric acid.

H. Schiff[2] investigated the reactions of other bases with furfurol, and found that various aromatic amines, amido acids and acid amides could take the place of aniline in this reaction. He always obtained a red or violet-colored product. Of the aliphatic amines only urea and allantoïn would take part in the reaction. Schiff concluded that furfurol, in contradistinction to the aromatic aldehydes, does not form the usual condensation-product with organic bases. Prof. Wallach and I[1] have, however, obtained these ordinary condensation-products with the different amines, according to the following reactions:

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[1] Ann. Chem. (Liebig) **156**, 197.

[2] Ibid. **201**, 355; **239**, 349.

$$R.NH_2 + C_5H_4O_2 = RN : C_5H_4O + H_2O, \text{ and}$$
$$2R' : NH + C_5H_4O_2 = (R'N)_2.C_5H_4O + H_2O.$$

Nevertheless, the bases which are the products of this condensation possess properties entirely different from those of the bases before mentioned, and in every way behave themselves like simple condensation-products, being very easily transformed back into aldehyde and base by the action of dilute acids or even by boiling with water. The decomposition of the dyes is not of such a simple character, and Schiff on this account concluded that they could not be simple condensation-products. Nor did he think their formation was to be explained by the view that there was a rupture of a double union in the furfurol nucleus, since aniline is not capable of uniting itself to the nucleus of pyromucic acid or its nitrogen derivatives. Heated with pyromucic acid and zinc chloride at 160° C., aniline yields as the only condensation-product pyromucanilide. That the oxygen atom of the furfuran nucleus took no part in the formation of the base, Schiff proved in like manner, drawing the conclusion that a furfuran-diphenylmethane nucleus is present in these dyes. He therefore put forward to represent the composition of furfuraniline, the formula[2]

$$CH\left\{\begin{matrix} C_4H_3O \\ C_6H_4.NH_2.HCl. \\ C_6H_4.NH_2.H_2O \end{matrix}\right.$$

This assumption is very plausible, but it must be remembered that Schiff could bring forward no proof of it, since he was unable to prepare the free furfuran-diphenylmethane.

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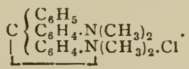
[1] *Vide* author's Inaug. Diss., Göttingen, 1891.

[2] There is, if this formula be correct, similarity between the formation of furfuraniline and that of leuco-malachite green from benzaldehyde and dimethylaniline in the presence of zinc chloride. Yet a tetramethylfurfuraniline salt would not be analogous to malachite-green, as can easily be seen by a comparison of the formulæ:

I. $CH\left\{\begin{matrix} C_4H_3O \\ C_6H_4.N(CH_3)_2.HCl. \\ C_6H_4.N(CH_3)_2.H_2O \end{matrix}\right.$

II. 

$C\left\{\begin{matrix} C_6H_5 \\ C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2.Cl \end{matrix}\right.$.

A compound which differs from leuco-malachite-green only in the fact that it contains, in the place of three benzene nuclei, two of benzene and one of furfuran, was prepared by Otto Fischer (Ann. Chem. [Liebig] **206**, 141) by heating furfurol with diphenylamine and zinc chloride: this compound is, however, colorless.

It therefore seemed to me worth while to test the formula proposed by Schiff. When working in the laboratory of the Johns Hopkins University, this investigation was begun, but the work was soon after unavoidably interrupted. I herewith publish such results as have been so far obtained, though I regret that I shall not be able to continue the work in the immediate future.

The simple condensation-products obtained by Wallach and myself can readily be distilled under diminished pressure: the dye-forming bases, on the other hand, cannot be distilled without decomposition, even in a vacuum. My results accord in this respect with the statements of Schiff. The preparation of the dye-forming bases in a pure condition was, after repeated attempts, given up. Schiff tried in vain to prepare the free furfuran-diphenylmethane, but as he had always worked with the base in the presence of water and as the latter substance reacts upon the dye-forming bases and their derivatives, decomposing them with ease, it seemed not impossible that in solutions free from water better results might be obtained. My first attempt was to diazotise the acetate by means of amyl nitrite, according to the method of Knoevenagel,[1] the acetate being moderately soluble in alcohol, especially in the presence of a little glacial acetic acid.

A solution of the acetate in absolute alcohol containing acetic acid was therefore treated with the theoretical amount of amyl nitrite. Even after standing 24 hours, there was no precipitation on the addition of ether. A small amount of a gummy product was gradually deposited, but this was insoluble in water and did not explode when heated on platinum foil. The color of the solution had, while standing, changed from a deep red to a dirty brown. No diazo-product could be isolated.

The method, devised by Liebermann and Scheidung[2] and improved by E. and O. Fischer,[3] by which the amido group may be directly replaced by a hydrogen atom, was also employed. The hydrochloric-acid salt of the toluidine compound was used, and this was ground, in small quantities at a time, with concentrated sulphuric acid. By this action there was formed a green solution which contained the base, still undecomposed, for the addition of alcohol restored the red color. This solution in sulphuric acid was then diazotised by means of nitrous acid and, on being mixed with absolute alcohol, the product gave rise to a

[1] Ber. d. chem. Ges. **23**, 2995.

[2] Ibid. **8**, 1108.

[3] Ibid. **9**, 899.

brisk evolution of nitrogen and aldehyde—a result Schiff also obtained in his attempts to form the diazo-compound. I was unsuccessful, as he was, in my attempts to obtain a neutral product from the alcoholic solution: the compound had suffered a deep-seated decomposition.

After having obtained these negative results, I determined to investigate the products of the decomposition of the substance more closely; this I have only begun.

In the formation of furfuraniline from furfurol, aniline and aniline hydrochloride there is no separation of water, as one would expect. Schiff repeatedly declares in his papers that there is no reason for believing water of crystallisation present in the base, but is of the opinion that it is combined with one of the amido groups.[1] As this supposition did not seem to me very probable, the paratoluidine compound was heated to a temperature of 100° to 105° C. The compound did not at first show any signs of decomposition, but after some hours began to give off a strong pungent odor. Constant weight was not reached after fourteen hours' heating, yet after a few hours the loss was slight.

1.4672 grams of base, twice recrystallised, was heated at 100°–105° C., and weighed at the end of each hour. During the eighth hour the loss in weight was 0.0011 gram; during the ninth, 0.0016 gram. During the nine hours the total loss in weight was 0.0793 gram = 5.40 per cent. One molecule of water would correspond to 5.17 per cent. The analysis of the dried substance gave the following results:

	Calculated for $C_{19}H_{20}N_2O.HCl$.	Found.	
		I.	II.
C	69.51	69.67	69.25
H	6.40	6.88	6.72

Examined with the microscope, the crystals, which had originally appeared well-formed, transparent, violet-colored needles, were found to have become shapeless and opaque, after being heated for nine hours. The violet color had changed to a reddish tint. The dried substance behaves itself towards solvents, however, precisely like the crystalline compound. It seems to me that these facts justify the view that water of crystallisation is present in the compound, and that the conception of water being combined with one of the amido groups is not supported in any way by the facts.

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[1] See Schiff's formula, p. 311.

The compound is decomposed by heating, the furfuran nucleus being broken down. Of the benzene nuclei one at least remains undecomposed. Furfuran-paratoluidine hydrochloride was heated in a tube at 200°, and yielded, in addition to dark-colored decomposition-products, colorless crystals. An aqueous extract yielded a precipitate with platinic chloride; with furfurol and acetic acid it became red. The product of the heating was therefore an aromatic base. It is then of the greatest importance, in order to establish the constitution of the dye-forming base, to determine which of the aromatic bases is here produced. If the view that the substance contains a furfuran-diphenylmethane nucleus be correct, we might expect to obtain a compound containing either a diphenylmethane nucleus, or, in the case of furfuran-toluidine, one containing two alkyl radicles in the place of benzene hydrogen atoms.

Furfurol has no action upon dimethylaniline or its hydrochloric-acid salt. From this Schiff concluded that in the formation of the dye, one molecule each of base and furfurol must at first unite, with splitting off of water, to form the usual condensation-product; this then combines with another molecule of base. Wallach and I have shown that the formation of these condensation-products with the aromatic bases does actually take place. If, then, the compound $C_6H_5.N:C_5H_4O$ can form with dimethylaniline a dye of the composition $CH\left\{\begin{array}{l}C_6H_4.NH_2\\ C_6H_4.N(CH_3)_2.HCl.H_2O\\ C_4H_3O\end{array}\right.$, this would be a strong argument in favor of Schiff's furfuraniline formula. This reaction I herewith desire to reserve for investigation.

THE TRANSPORTATION OF SOLIDS IN A VACUUM BY THE VAPORS OF METALS.

BY H. N. MORSE AND JOHN WHITE, JR.

Further experiments[1] on the transportation of substances in a vacuum by the vapors of zinc, cadmium and magnesium have shown us that our explanation of the phenomenon was entirely erroneous.

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[2] This Journal **11**, 258, 348.

It has since been found that other substances than the oxides and sulphides, such as barium carbonate and powdered porcelain can be transported with equal facility and without change of composition; moreover, that the insertion of porous plugs of asbestus, which allow the metallic vapors to pass, will effectually stop all the solids which were experimented with. It appears, therefore, that the transportations which we described must have been of a mechanical nature, and not due to dissociation.

We have also examined with greater care the gas which is evolved when the oxides of zinc, cadmium and magnesium are heated in a vacuum with their respective metals, and found it to be quite pure nitric oxide. In the original experiments the oxides were heated to redness in a vacuum, until they ceased to give off gas, before heating them with the metals. This precaution, it now appears, did not suffice for the complete decomposition of the small quantities of nitrate which they contained. Zinc oxide which has been heated to a high temperature in a muffle-furnace, does not give up any gas when heated with metallic zinc in a vacuum. The gas which was liberated when the oxides and metals were heated together was found to be insoluble in strong caustic potash, but readily soluble in an alkaline solution of pyrogallic acid; it was therefore too hastily concluded that the gas must be oxygen. In our later experiments this gas was found to be indifferent to phosphorus, but readily absorbed by solutions of ferrous salts. It appeared, furthermore, that freshly prepared alkaline solutions of pyrogallic acid absorb nitric oxide with considerable avidity.

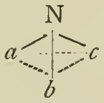
To determine whether nitric oxide is readily reduced by the vapors of metallic zinc, we exhausted a tube containing some of the metal, and then filled it with the oxide. After heating the tube in a combustion-furnace for six hours, the contents were pumped out and examined. About ninety-five per cent. of the gas thus obtained was unchanged nitric oxide. In the light of this result it is easy to understand why the gas which is rapidly pumped off when zinc and zinc oxide containing some nitrate are heated together in a vacuum, should consist of pure nitric oxide, instead of a mixture of its reduction-products.

REVIEWS AND REPORTS.

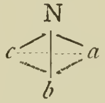
STEREOCHEMISTRY.

II.—*The Stereochemistry of Nitrogen.*[1]

The first founder of stereochemistry was also the first to suggest a three-dimensional arrangement of the radicles attached to nitrogen. Van't Hoff[2] bases this arrangement on the fact that of the five valences of nitrogen three are apparently alike, while two differ from these in that they are active only in exceptional cases. That the three ordinary valences are alike is shown by the fact that among complex ammonias (N.*a*.*b*.*c*) there is no isomerism. This indicates that *a*, *b*, *c* are in the same plane with N; for otherwise we should have two formulæ,



and



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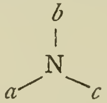
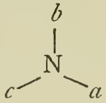
which are non-superposable and represent therefore two distinct substances; whereas the plane formulæ



and



,

being superposable, are identical.

The arrangement of *a*, *b* and *c* round N is then that of the corners of an equilateral triangle round its center; always remembering that the nitrogen triangle is represented as equilateral for the same reason that the carbon tetrahedron is represented as regular, not because we know the different radicles to be at the same distance from the connecting element, but because we know not which is nearer and which farther from it.

As to the positions of the radicles *d* and *f*, bound by the two supplementary valences, we have no reason to suppose that either of these is nearer to any one of the radicles *a*, *b*, *c* than to the others. The radicles *d* and *f* must therefore be represented as equidistant from each of the three radicles *a*, *b*, *c*; so that the arrangement is determined by the position of five points, three of which are equidistant from one another and from each of the other two. Now three points cannot be equidistant from each of two other points which are in the same plane with them; hence a three-dimensional arrangement is necessary. The arrangement is shown in perspective in Fig. 1, and more clearly perhaps in Fig. 2; here 1, 2, 3 are the ordinary similar valences and 4 and 5 the supplementary valences. The fact that 4 and 5 are dissimilar in that one binds negative and the other positive radicles might be represented by using a + and a — sign.[1] It cannot be represented by making one line longer than the other, because the difference is a difference of kind, not of degree merely.

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[1] For "Stereochemistry of Carbon" see This Journal **13**, 496, 573; **14**, 58.

[2] Ansichten über die organische Chemie (Brunswick, 1881), p. 79

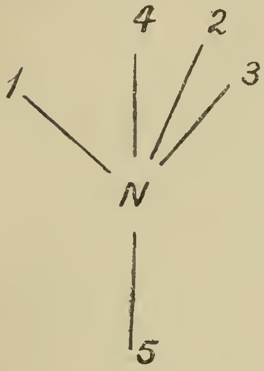

FIG. 1.

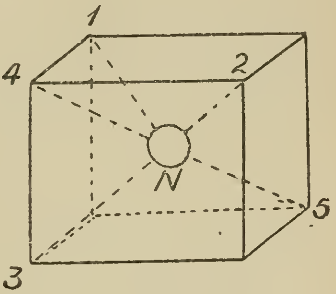

FIG. 2.

Now we have experimental proof that the arrangement of five radicles attached to nitrogen is a three-dimensional one. Le Bel[2] obtained by the action of ferments on methyl-ethyl-propyl-isobutyl-ammonium chloride, $\left.\begin{array}{l}CH_3\\C_2H_5\\C_3H_7\\C_4H_9\end{array}\right\}NCl$, a solution optically active.[3] That is to say, the molecule in question has no plane of symmetry; therefore its components cannot all be grouped in a single plane.

Again, Van't Hoff's configuration demands the existence of two isomers NA_3BC (or NA_2B_2C), for if C occupy bond 5 (Fig. 1), bond 4 may be occupied by either B or A. In the case of dimethyl-diethyl ammonium iodide, $N(Me)_2Et<\begin{smallmatrix}Et\\I\end{smallmatrix}$, and $NMe(Et)_2<\begin{smallmatrix}Me\\I\end{smallmatrix}$, there is said to be no isomerism.[4] The Figs. 3 and 4, which represent the theoretical isomers, have, however, the same plane of symmetry which may determine the identity in crystalline form; hence Van't Hoff demands further evidence of the alleged identity.

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[1] Compare Behrend: Ber. d. chem. Ges. **23**, 454 and 1776; and Willgerodt's objections, J. prakt. Chem. [2] **41**, 526.

[2] Bull. Soc. chim. (Paris) [3] **4**, 613.

[3] According to this, Le Bel's view that the essential condition for the optical activity of an organic substance in solution is the presence of any asymmetric molecule must be preferred to Van't Hoff's theory that the presence of an asymmetric carbon atom is essential.

[4] V. Meyer and Lecco: Ber. d. chem. Ges. **7**, 1747; **8**, 223 and 936.

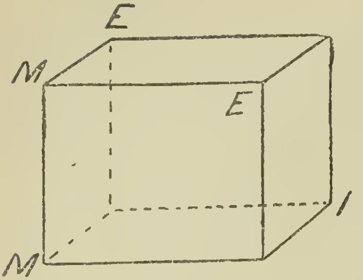

FIG. 3.

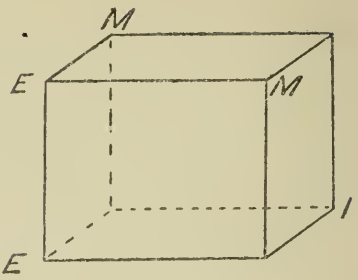

FIG. 4.

And in a parallel case, that of triethyl-benzyl-ammonium iodide, Ladenburg[1] proved in his noted controversy with Victor Meyer[2] that two isomers exist and ascribed to them the formulæ

$$N(C_2H_5)_3<{}^{C_6H_5.CH_2}_{I} \text{ and } N(C_2H_5)_2C_6H_5.CH_2<{}^{C_2H_5}_{I}.$$

A difference between the substances to which these formulæ were assigned has been observed by Le Bel[3] also; and the case has been duplicated by his discovery of two isobutyl-trimethyl-ammonium chlorides.[4]

Van't Hoff's speculations foreran contemporary chemistry, so that by the time other chemists began to entertain similar views they had forgotten the original statement of them. Thus Willgerodt,[5] to whom Van't Hoff's work was evidently unknown, gave as the general formula for nitrogen compounds a solid figure derived from Fig. 1 by simply joining together the points 1, 2, 3 and joining 4 and 5 to these, forming the outline of the figure given for two carbons trebly-linked.[6] This Willgerodt called the nitrogen double-tetrahedron.

It is needless to discuss Willgerodt's explanation of certain cases of isomerism among derivatives of azobenzene said to be structurally identical, because the structural identity is apparently unproven,[7] and because the explanation itself admittedly[8] requires to be explained.

The two supplementary valences (*Burch and Marsh*).—The expression of the fact that nitrogen, which can bind five, so often binds only three monads, we have seen in Van't Hoff's formulæ; we have now to consider the explanation of this fact. An explanation of the general phenomenon of varying valence is given by Van't Hoff in the introduction to his *Ansichten*, and would be expressed in a nitrogen formula by making the distance N4 (= N5) greater than the distance N1 (= N2 = N3), Fig. 1. For the particular case of nitrogen an explanation (which may possibly be extended to other elements) has been suggested by Burch and Marsh:[1] the valences apparently latent may in reality be engaged in binding together nitrogen atoms belonging to what are at present regarded as different molecules.

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[1] Ber. d. chem. Ges. **10**, 43, 561, 1152 and 1634.

[2] Ibid. **10**, 309, 964, and 1291.

[3] Bull. Soc. chim. (Paris) [3] **3**, 244, and **4**, 104.

[4] Compt. rend. **110**, 144.

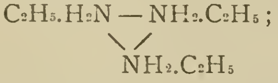
[5] J. prakt. Chem. [2] **37**, 449; also **41**, 291, and **42**, 127.

[6] This Journal **13**, 580.

[7] Kehrmann and Messinger: Ber. d. chem. Ges. **25**, 598.

[8] Willgerodt: loc. cit. **37**, 452.

The molecule of ethyl-amine would then be not $NH_2.C_2H_5$, but a multiple of this, such as $C_2H_5.H_2N = NH_2.C_2H_5$ or



$$C_2H_5.H_2N - NH_2.C_2H_5;\quad \underset{NH_2.C_2H_5}{\diagdown\diagup}$$

and if these complex molecules are dissociated by rise of temperature, the vapor of ethyl-amine should give abnormally large expansion on heating. Experiment showed an expansion 5 to 6 per cent. in excess of the normal, with contraction to the original volume on cooling. The impossibility of separating by fractional distillation mon-ethyl-, di-ethyl- and tri-ethyl-amine is due perhaps to the linking together of the different compounds by the supplementary nitrogen-valences.

Now carbon, which in combination is remarkable for the linking together of numbers of its own atoms, exhibits similar linking when free; so also with sulphur.[2] Accordingly the proof given by Burch and Marsh, that pentad nitrogen when combined has something of the self-binding power possessed by carbon and sulphur, stands in direct connection with the remarkable work of Stillingfleet Johnson,[3] whose conclusions have received independent corroboration from Thomson and Threlfall,[4] and whose researches make it probable that nitrogen when free may be formed into molecules containing more atoms than the ordinary nitrogen molecule. For the abnormal *contraction* which Thomson and Threlfall observed on passing the electric discharge through gaseous nitrogen, may be due to triad nitrogen becoming pentad,[5] just as the abnormal *expansion* of ethyl-amine vapor is said to be due to pentad nitrogen becoming triad. The stereochemical bearing of these arguments becomes clear when we consider that Van't Hoff's nitrogen figure contained within itself the prediction that the molecule of Johnson's allotropic nitrogen (if this is indeed pentad nitrogen), like the molecule, or rather the various molecules of carbon, must consist of more than two atoms, for with pentad nitrogen, as with carbon, the direction of the valences is

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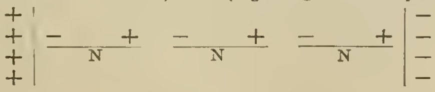
[1] J. Chem. Soc. **55**, 654.

[2] Van't Hoff: "Ansichten," p. 23.

[3] J. Chem. Soc. **39**, 128, 130; also "Elementary Nitrogen," London: Churchill, 1885.

[4] Proc. Roy. Soc. **40**, 329.

[5] Accepting the pole hypothesis as to the supplementary valences, the explanation of their *Activirung* would be that the opposite poles are brought into proximity by the difference of potential between the surfaces A and B; thus: (neglecting the ordinary valences)—



such that all cannot be satisfied by the union of two atoms; whereas in molecules composed of triad nitrogen the union of two atoms may evidently satisfy all the valences.

The three ordinary valences (*Hantzsch and Werner*).—With the publication in 1890 of a paper by Hantzsch and Werner[1] the stereochemistry of nitrogen entered on a new phase. Their theory, like the stereochemical theories of Van't Hoff, arose from the consideration of certain cases of unexplained isomerism. The isomers in question were aromatic oximes, such as the oxime of benzaldehyde, $C_6H_5.CH:NOH$, which exists in two chemically distinct forms of the same structural formula. To explain this Hantzsch and Werner began by denying that the three ordinary nitrogen valences always occupy the same plane; in cyanogen —CN and pyridin $C_5H_5\vdots N$ the carbon valences linked with nitrogen not being in the same plane, it follows that the nitrogen valences themselves must be out of plane; in certain compounds, then, the three valences of nitrogen are directed towards three apices of a (doubtless irregular) tetrahedron, the fourth apex of which is occupied by the nitrogen atom.

From this arrangement it follows that three classes of stereoisomers are possible:

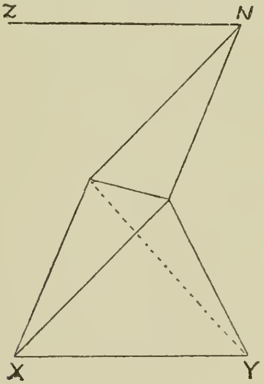


FIG. 5.

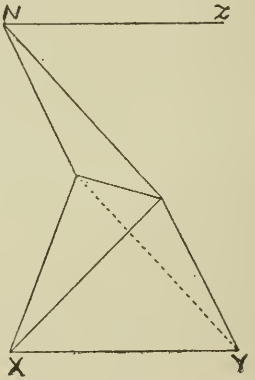


FIG. 6.

I. Type $\begin{array}{c}\text{Z.N}\\ \|\\ \text{X.C.Y}\end{array}$ and $\begin{array}{c}\text{N.Z}\\ \|\\ \text{X.C.Y}\end{array}$ (Figs. 5 and 6), analogous to $\begin{array}{c}\text{H.C.Z}\\ \|\\ \text{X.C.Y}\end{array}$ and $\begin{array}{c}\text{Z.C.H}\\ \|\\ \text{X.C.Y}\end{array}$.

Examples: Benzaldoximes $\begin{array}{c}\text{H.C.}C_6H_5\\ \|\\ \text{N—OH}\end{array}$ and $\begin{array}{c}\text{H.C.}C_6H_5\\ \|\\ \text{HO—N}\end{array}$.

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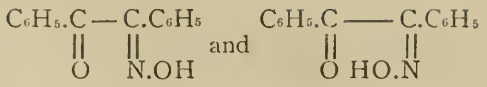
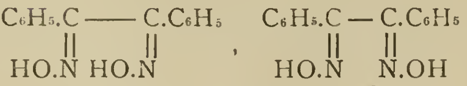
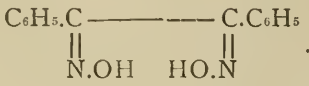
[1] Ber. d. chem. Ges. **23**, 11.

Benzilmonoximes  $\begin{matrix}C_6H_5.C & — & C.C_6H_5\\ \| & & \|\\ O & & N.OH\end{matrix}$ and $\begin{matrix}C_6H_5.C & — & C.C_6H_5\\ \| & & \|\\ O & & HO.N\end{matrix}$.

α γ

Benzildioximes  $\begin{matrix}C_6H_5.C & — & C.C_6H_5\\ \| & & \|\\ HO.N & & HO.N\end{matrix}$, $\begin{matrix}C_6H_5.C & — & C.C_6H_5\\ \| & & \|\\ HO.N & & N.OH\end{matrix}$ and

α β

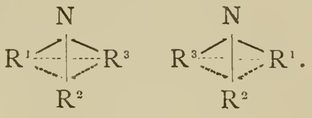


$\begin{matrix}C_6H_5.C & — & C.C_6H_5\\ \| & & \|\\ N.OH & & HO.N\end{matrix}$.

γ

II. Type $\begin{matrix}N.X\\ \|\\ N.Y\end{matrix}$ and $\begin{matrix}N.X\\ \|\\ Y.N\end{matrix}$ analogous to $\begin{matrix}(CH).X\\ \|\\ (CH).Y\end{matrix}$ and $\begin{matrix}(CH).X\\ \|\\ Y.(CH)\end{matrix}$.

No examples yet known with certainty.

III (*a*). Type N.X.Y.Z 

(*b*). Type $\begin{matrix}X.N.Y\\ |\\ U.N.Z\end{matrix}$ and $\begin{matrix}X.N.Y\\ |\\ Z.N.U\end{matrix}$

No examples known.

The scarcity of $\begin{matrix}N\\ \|\\ N\end{matrix}$–isomers (Group II. above) is less striking if we consider that $\begin{matrix}CHCl\\ \|\\ CHCl\end{matrix}$ and $\begin{matrix}CH.C_6H_5\\ \|\\ CH.C_6H_5\end{matrix}$ occur each in one form only, while $\begin{matrix}C.C_6H_5.Cl\\ \|\\ C.C_6H_5.Cl\end{matrix}$ has two forms; i. e., simultaneous accumulation of negative and of phenyl (aromatic) groups favors occurrence of isomerism among carbon derivatives (as among the nitrogen compounds of Group I—the oximes); whereas, even among carbon derivatives isomers may be lacking in compounds possessing analogous constitution, but lacking the right combination of groups.

As to the absence of isomers of Group III (NXYZ), this is accounted for by the theory that the three nitrogen valences are all in one plane except when diverted by special cause. If in any case such special cause exists, optically active isomers[1] may be expected.[2] Thus Hantzsch and Werner give a general theory leading us to expect the occurrence of those cases of isomerism which actually exist, but also of many others; and then to account for the non-existence of these latter, they give special subsidiary theories.

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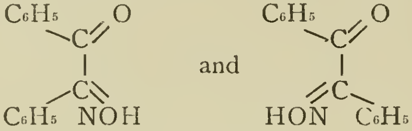
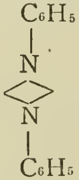
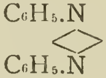
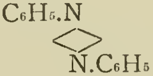
[1] Bischoff is trying to prepare such isomers: Ber. d. chem. Ges. **23**, 1967.

[2] See ante, p. 316.

Opposition to the theory arose from the belief that not the presence of nitrogen but the presence of two singly-linked carbons was the necessary condition for the occurrence of isomerism among structurally identical oximes, and the formulæ



had been proposed by Auwers and Meyer,[1] who thought that in this case relative rotation[2] of the singly-linked carbon atoms did not take place. As to the benzaldoximes, these, it was said, were structurally, not stereochemically, different. The improbability of the latter assertion has been demonstrated by the work of Goldschmidt[3] and of Hantzsch,[4] as Meyer[5] now admits; and the former theory was crushed by the discovery of structurally identical ketoximes containing no $\begin{array}{c}C\\|\\C\end{array}$ group, viz. the oximes of parachlorbenzophenone, $C_6H_5.CO.C_6H_4.Cl$, discovered by Auwers and Meyer[6] themselves, and others discovered by Hantzsch.[7]

Meyer, however, had based his opposition on other grounds also, maintaining[8] that though the three valences of nitrogen may be diverted from one plane by adequate force, such force is lacking in cases where Hantzsch and Werner base their theory on its existence; that it is the absence of any such diverting force (and not the absence of negative groups) which accounts for the fact that azo-benzene exists in but one form, viz.  $\begin{array}{c}C_6H_5\\|\\N\\<\!\!>\\N\\|\\C_6H_5\end{array}$, and not in the two forms  $\begin{array}{c}C_6H_5.N\\<\!\!>\\C_6H_5.N\end{array}$ and  $\begin{array}{c}C_6H_5.N\\<\!\!>\\N.C_6H_5\end{array}$ (see isomers of type

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[1] Auwers: "Entwicklung der Stereochemie," p. 53 et seq.; see also Meyer: Ber. d. chem. Ges. **23**, 592.

[2] See ante, **14**, 59.

[3] Ber. d. chem. Ges. **22**, 3109, and **23**, 2163, 2746. For Beckmann's papers on the subject see Ibid. **20**, 2766; **22**, 429, 514, 1531, 1588; **23**, 1680, 3319, 3331.

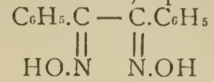
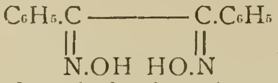
[4] Ibid. **24**, 13.

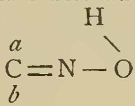
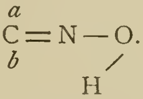
[5] Ann. Chem. (Liebig) **264**, 16.

[6] Ber. d. chem. Ges. **23**, 2063.

[7] Ibid. **23**, 2322.

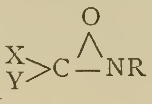
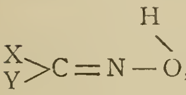
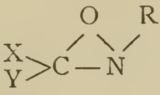
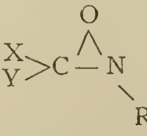
[8] Ibid. **23**, 607.

II above). Further, where there is force adequate to cause divergence, the direction in which it acts is constant; so that, in the case of benzil-dioxime, if phenyl attracts hydroxyl, the formula would be only  $\begin{array}{ll} C_6H_5.C & - C.C_6H_5 \\ \quad\| & \quad\| \\ HO.N & N.OH \end{array}$; and if phenyl repels hydroxyl, the formula could be only  $\begin{array}{ll} C_6H_5.C & ——— C.C_6H_5 \\ \| & \qquad\quad\| \\ N.OH & \qquad HO.N \end{array}$; in either case, therefore, we have but one formula for the oxime.

Hantzsch and Werner[1] admit that since the three nitrogen valences are originally in one plane there must be in the ketoximes a special cause for their divergence, but the divergence need not be always in the same direction, for in the formation of a ketoxime addition first takes place: $>C = O + H_2N.OH = >C<^{OH}_{NH.OH}$; and the hydroxyl so formed may take the place which would otherwise be taken by the hydroxyl of the hydroxylamine; this latter hydroxyl is thus forced into an unfavorable position, in which it may remain even after the splitting off of H_2O. But again Auwers and Meyer[2] objected that the isomerism, the production of which is ascribed to nitrogen, occurs only among hydroxyl-amine derivatives, and may be better accounted for by the formulæ  $\overset{a}{\underset{b}{C}}=N-\overset{\overset{H}{\diagdown}}{O}$ and  $\overset{a}{\underset{b}{C}}=N-\underset{\underset{H}{\diagup}}{O}.$

These formulæ were met by several counter-objections[3] which seem fatal. Thus:

1. They do not represent two distinct molecules, but two phases in the rotation of the atoms of the same molecule; for why should not H rotate round $=N-O-$?

2. The existence of two structurally identical nitrogen-ethers is unexplained;  ${}^{X}_{Y}\!>C\overset{\overset{O}{\diagup\diagdown}}{—}NR$ cannot be derived in two forms from  ${}^{X}_{Y}\!>C=N-\overset{\overset{H}{\diagdown}}{O}$, whereas by diverting the nitrogen valences we have at once  ${}^{X}_{Y}\!>C-\overset{\overset{O\quad R}{\diagup\diagdown\diagup}}{N}$ and  ${}^{X}_{Y}\!>C\overset{\overset{O}{\diagup\diagdown}}{—}\underset{\underset{R}{\diagdown}}{N}$.

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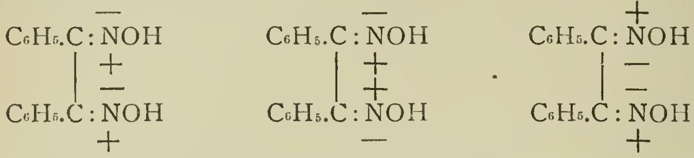
[1] Ber. d. chem. Ges. **23**, 1243.

[2] Ber. d. chem. Ges. **23**, 2403.

[3] Hantzsch and Werner: Ibid. **23**, 2764. See also Ibid. **24**, 3511, and the answer of Auwers and Meyer: **24**, 4226.

The theory of Behrend is also discussed by Hantzsch and Werner. Behrend[1] assumes the existence in the nitrogen atom of two poles of opposite sign (corresponding to the two supplementary valences) and ascribes to the three benzil-dioximes the formulæ



$$\begin{array}{c} C_6H_5.C:\overset{-}{NOH} \\ |\ \begin{matrix}+\\-\end{matrix} \\ C_6H_5.C:\underset{+}{NOH} \end{array} \qquad \begin{array}{c} C_6H_5.C:\overset{-}{NOH} \\ |\ \begin{matrix}+\\+\end{matrix} \\ C_6H_5.C:\underset{-}{NOH} \end{array} \qquad \begin{array}{c} C_6H_5.C:\overset{+}{NOH} \\ |\ \begin{matrix}-\\-\end{matrix} \\ C_6H_5.C:\underset{+}{NOH} \end{array}$$

But this theory also is rejected; for, *inter alia*, it fails to account for the isomerism of the benzaldoximes.

Besides combatting the opinions of others, Hantzsch and Werner have sought positive evidence in favor of their own, and this in two ways: Firstly, by trying to prepare the isomers foreseen by their theory; secondly, by trying to obtain the reactions which the theory attributes to each isomer.

I. *a.* Isomers other than oximes have been found only among the hydrazones[2] $\begin{array}{l} XCY \\ \| \\ N-NH.C_6H_5 \end{array}$ and $\begin{array}{r} XCY \\ \| \\ C_6H_5.HN-N \end{array}$.

Substances such as N.X.Y.Z and $\underset{Y}{\overset{X}{C}}=\overset{Z}{N}$ could not be prepared in more than one form. Thus Kraft[3] tried in vain to break up ethyl-toluidine, $N\begin{cases} C_2H_5 \\ CH_2.C_6H_6 \\ H \end{cases}$, into two optically active isomers; but he found that the method tried—the crystallisation of the tartrate in presence of coniine tartrate—was unsuccessful also when applied to an inactive base containing an asymmetric carbon atom, so that the experiment shows only the difficulty, not the impossibility, of obtaining isomeric ammonia derivatives.

b. Among oximes space-isomerism is possible if the radicles attached to $>C=N.OH$ are any two of the following: H, C_6H_5, C_4H_3O, C_4H_3S, $CH_3.C_6H_4$, $C_6H_4.Cl$, $C_2H_3O.C_6H_4$.[4] Methyl, and probably alkyls generally prevent this isomerism.[5]

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[1] See ante, p. 316.

[2] Ber. d. chem. Ges. **23**, 2769; **24**, 3511. Compare Auwers and Meyer and their collaborators, Ibid. **23**, 1574, 3617; **24**, 4225.

[3] Ibid. **23**, 2780. Compare Bischoff, Ibid. **23**, 1967.

[4] To these must be added a variety of others if Werner (Ber. d. chem. Ges. **25**, 27) is right in explaining the isomerism observed among hydroxamic acid derivatives according to his theory. There are at least twenty-seven of these compounds which occur in more than one modification (Lossen: Ber. d. chem. Ges. **25**, 433); but Lossen finds that some of these occur in three modifications, and, besides, he distrusts the methods by which Werner arrives at his conclusions.

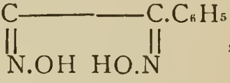
[5] Kehrmann (J. prakt. Chem. [2] **42**, 134) had suggested that the reason V. Meyer could not prepare isomeric diacetyl-dioximes was because in the process of formation the unfavored turns into the favored configuration, while the more unwieldy benzil-derivatives require stronger impulses to effect conversion. But Hantzsch says it is not so much the space occupied by the radicles which is of moment as their configuration, a factor at present undetermined. For the oxime of benzaldehyde exists in two forms, that of aceto-phenone in one form only, although the latter has in place of hydrogen the larger methyl.

II. *a.* Of two aldoximes, $\begin{matrix}\text{XCH}\\ \| \\ \text{N.OH}\end{matrix}$ and $\begin{matrix}\text{X CH}\\ \| \\ \text{HO.N}\end{matrix}$, the former should yield the nitrile $\begin{matrix}\text{XC}\\ ||| \\ \text{N}\end{matrix}$ more readily than the latter. Experiment confirms this.[1]

b. To ketoximes Beckmann's transformation was applied—a transformation which may take place in either of two ways: $\begin{matrix}X\\Y\end{matrix}\!\!>C=N.OH \rightarrow X.\underset{O}{C}-N<^{H}_{Y}$ or $Y.\underset{O}{C}-N<^{X}_{H}$. Whether it is X or Y which changes its place should depend on which is nearer to the hydroxyl:

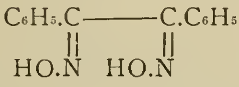
$$\begin{matrix}X\\Y\end{matrix}\!\!>C=\overset{OH}{N} \rightarrow Y\overset{O}{C}-\overset{X}{N}H;\ \text{and}\ \begin{matrix}X\\Y\end{matrix}\!\!>C=\underset{OH}{N} \rightarrow X\underset{O}{C}-\underset{Y}{N}H.$$

And of the three benzil-dioximes— I.



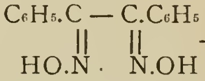
$$\begin{matrix}C_6H_5.C & \text{———} & C.C_6H_5\\ \| & & \| \\ \text{N.OH} & & \text{HO.N}\end{matrix},$$

II.



$$\begin{matrix}C_6H_5.C & \text{———} & C.C_6H_5\\ \| & & \| \\ \text{HO.N} & & \text{HO.N}\end{matrix},$$

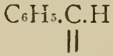
III.



$$\begin{matrix}C_6H_5.C & — & C.C_6H_5\\ \| & & \| \\ \text{HO.N} & & \text{N.OH}\end{matrix}$$

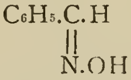
— that one (III) which the least readily yields the anhydride should the most readily undergo the transformation of Beckmann. This also is confirmed by experiment.[2]

To distinguish structurally identical nitrogen compounds $\begin{matrix}\text{X.C.Y}\\ \| \\ \text{Z.N}\end{matrix}$ and $\begin{matrix}\text{X.C.Y}\\ \| \\ \text{N.Z}\end{matrix}$ by name Hantzsch[3] uses the prefixes *syn-* and *anti-*, which indicate the position of the radicle Z with regard to that one of the radicles X and Y which is capable of intramolecular reaction with Z and the name of which is to immediately follow the prefix. Thus:



$$\begin{matrix}C_6H_5.C.H\\ \| \\ \text{HO.N}\end{matrix}$$

Benz-anti-aldoxime.

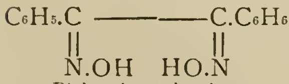


$$\begin{matrix}C_6H_5.C.H\\ \| \\ \text{N.OH}\end{matrix}$$

Benz-syn-aldoxime.

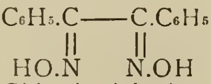
In the case of dioximes the prefixes refer to the two hydroxyl groups, and where these have the asymmetrical position the term *amphi-* is used.

The oximes of diphenyl-glyoxal are then



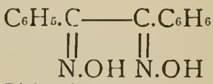
$$\begin{matrix}C_6H_5.C & \text{———} & C.C_6H_6\\ \| & & \| \\ \text{N.OH} & & \text{HO.N}\end{matrix}$$

Diphenyl-syn-glyoxime.



$$\begin{matrix}C_6H_5.C & \text{——} & C.C_6H_5\\ \| & & \| \\ \text{HO.N} & & \text{N.OH}\end{matrix}$$

Diphenyl-anti-glyoxime.



$$\begin{matrix}C_6H_5.C & \text{——} & C.C_6H_6\\ \| & & \| \\ \text{N.OH} & & \text{N.OH}\end{matrix}$$

Diphenyl-amphi-glyoxime.

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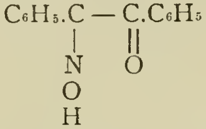
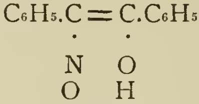
[1] Ber. d. chem. Ges. **23**, 25; **24**, 18. [2] Ibid. **24**, 23. [3] Ibid. **24**, 3479.

Hantzsch and Werner have done for the stereochemistry of nitrogen what Wislicenus did for the stereochemistry of carbon. They have rendered possible a systematic experimental investigation of the subject, and have themselves already pushed this investigation in many directions. Their theory is at present in possession of the field; but not in undisputed possession. Its origin was, as we have seen, due to the alleged existence of isomerism among structurally identical oximes, especially benzil-oximes. Now Claus[1] maintains that structurally identical benzil-oximes do not exist, and suggests the formulæ



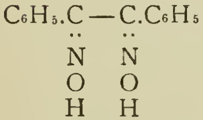
$$\begin{array}{cc} C_6H_5.C & - \; C.C_6H_5 \\ | & \| \\ N & O \\ O & \\ H & \end{array}$$

α-monoxime.



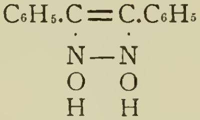
$$\begin{array}{cc} C_6H_5.C & = \; C.C_6H_5 \\ \cdot & \cdot \\ N & O \\ O & H \end{array}$$

γ-monoxime.



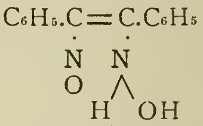
$$\begin{array}{cc} C_6H_5.C & - \; C.C_6H_5 \\ \cdot\cdot & \cdot\cdot \\ N & N \\ O & O \\ H & H \end{array}$$

α-dioxime.



$$\begin{array}{cc} C_6H_5.C & = \; C.C_6H_5 \\ \cdot & \cdot \\ N & - \; N \\ O & O \\ H & H \end{array}$$

β-dioxime.

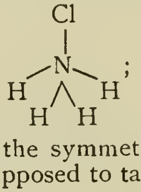


$$\begin{array}{ccc} C_6H_5.C & = \; C.C_6H_5 & \\ \cdot & \cdot & \\ N & N & \\ O & \wedge & \\ & H & OH \end{array}$$

γ-dioxime.

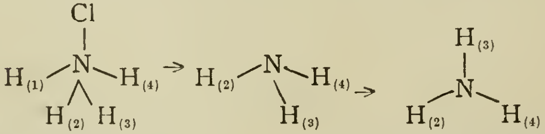
This suggestion threatens the very base of the whole theoretical structure built up by Hantzsch and Werner, Auwers and Meyer. The latter[2] seek to prove that the threat is vain, but are constrained to admit that stereochemistry has not yet shown why the more stable of the two benzil-monoximes should on further treatment with hydroxylamine yield the most unstable of the three dioximes (γ-monoxime yields γ-dioxime, see ante, p. 321). Their opposition has been met by Claus,[3] who promises experiments on the subject shortly.

Further, the Hantzsch-Werner theory does not cover the whole field. The problem of quinquivalent nitrogen is untouched by it. On this Bischoff[4] promises investigations, and suggests for NH_4Cl a formula in which the four hydrogen atoms are disposed at the base of a pyramid of which the chlorine occupies the apex—



;

while for NH_3 he retains the symmetrical formula in a single plane. The transition is supposed to take place thus:



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[1] J. prakt. Chem. [2] **44**, 312.

[2] Ber. d. chem. Ges. **24**, 3267.

[3] J. prakt. Chem. **45**, 1, and 377.

[4] Ber. d. chem. Ges. **23**, 1967.

Vaubel[1] has attacked the problem in a new way. He assumes that the carbon atom has the form of a regular tetrahedron, and that the atoms of all elements have the same specific gravity, so that the volume of the nitrogen atom is to that of the carbon atom as the atomic weight 14 is to the atomic weight 12. Calling the side of the carbon tetrahedron unity, its volume is $\frac{1}{12}$, and the volume of the nitrogen atom therefore $\frac{1}{12} \times \frac{14}{12} = \frac{7}{72}$. Further, in order that the nitrogen atom may replace a carbon atom in the benzene ring (Baeyer's rejected formula[2]) it must have an angle of 60° and sides equal to those of the carbon tetrahedron; and in order that it may replace two carbons in the ring (see Fig. 11) it must have a side equal to 1.732. To satisfy these hypotheses (which we will not here discuss) Vaubel proposes the form of which side-views are shown in Figs. 7 and 8.

Another view is seen in the formula for NH_4Cl (Fig. 9).

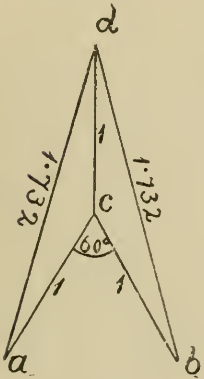

FIG. 7.

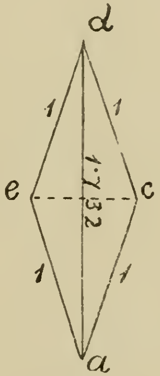

FIG. 8.

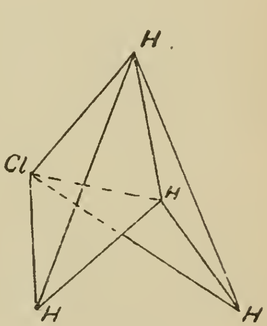

FIG. 9.

A number of illustrations are given by Vaubel to show how the form chosen is adapted to represent the linkage of nitrogen in various compounds; the formulæ for the $C \equiv N —$ group and for pyrrol will convey a sufficient idea of this. (Figs. 10 and 11.)

It will be seen that the division into three ordinary valences (*A*, *B*, *D*; Fig. 7) and two supplementary valences (*E*, *C*) is retained; but seeing that the supplementary are presumably weaker than the ordinary valences, it is unfortunate that the formula should represent *E* and *C* as nearer to the center of gravity of the atom than *A*, *B* and *D*.

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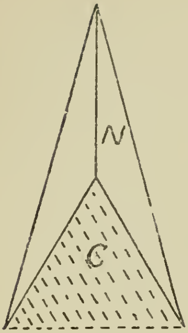
[1] "Das Stickstoffatom." Giessen: E. Ottmann, 1891.

[2] The formula (which Vaubel published as new in 1891 [J. prakt. Chem. [2] **44**, 137]) was proposed by Baeyer in 1888 (Ann. Chem. (Liebig) **245**, 124), only to be rejected by him in favor of the formula shown in Plate I. (ante Vol. 13 opposite p. 578). Either formula lends itself to the argument given above. The origination of the formula shown in the plate is mistakenly attributed by Vaubel to Loschmidt.



$C\equiv N-$

FIG. 10.

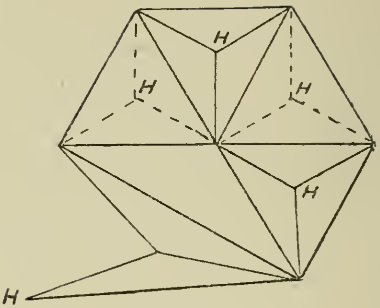


FIG. 11.

Conclusion.

The progress of the stereochemistry of nitrogen is naturally slow, owing to the relatively few cases of unexplained isomerism among nitrogen compounds; it is aided, however, by the knowledge already gained as to the stereochemistry of carbon, which has proved a useful guide in the search for new nitrogen isomers.

These outlines of stereochemistry cannot close without mentioning that, of the chemists who have considered the subject on general grounds, some have accorded but faint praise to such speculations; others, a more emphatic form of condemnation. Berthelot[1] maintained that it was of little use to theorise as to atomic arrangement without taking atomic motion into account; Kolbe[2] scoffed; Fittica[3] despaired. Claus[4] considers that while the physical properties of a substance depend to some extent on the arrangement of the atoms in the molecules, the evidence is altogether insufficient to show that, as regards chemical properties, this factor is of any weight compared with the specific nature of the atoms. Ostwald[5] admits that we are justified in attempting to explain the chemical properties of molecules by the arrangement of their atoms, but thinks[6] the question so complicated that this will prove to be but one factor among many; that we shall therefore more rapidly gain an insight into the problem of isomerism if we abandon geometrical representations and confine ourselves to "clear and necessary hypotheses."

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[1] Bull. Soc. chim. (Paris) [2] **23**, 338.

[2] J. prakt. Chem. [2] **15**, 473; **23**, 489.

[3] "The form and arrangement of atoms will probably remain for ever unknown."—Jahresbericht, 1888, p. 87.

[4] J. prakt. Chem. [2] **42**, 266; **45**, 12.

[5] "Grundriss der allgemeinen Chemie" (Leipzig: Engelmann, 1889), p. 206.

[6] Ztsch. phys. Chem. **9**, 220.

Note.

Books.—A bibliography is in preparation. For the work on carbon, Van't Hoff's " Dix années,"[1] or its translation[2] by Marsh, is of most importance to the student. These reports, which aim at supplying only the briefest possible review of the whole subject, will be reprinted in pamphlet form in the hope that they may prove useful as a text-book.

Models.—No nitrogen models are at present in general use. For private study, the carbon models made by joining four short pieces of rubber-tubing to a common center, and supplied by Schneck, Königsberger, and Mandl, Breitensee near Vienna, are very good.

The models (" solid formulæ ") which I recently described[3] will be supplied according to samples approved by me by Messrs. James Queen & Co., Chestnut Street, Philadelphia.

ARNOLD EILOART.

NOTES.

A. W. von Hofmann.

August Wilhelm von Hofmann, the distinguished professor of chemistry in the University of Berlin, died on the 5th of May. He was born April 8, 1818, in Giessen, a city that will always be remembered as the seat of that first chemical laboratory in which Liebig wrought such great results. Hofmann entered the University of Giessen in 1836 without a clear plan as to his future work. He soon, however, turned to the law, and later became interested in chemistry, probably through the influence of Liebig. He was a student of Liebig and afterwards his assistant. His first investigation was published in 1841, and treated of the volatile bases of coal-tar. In this work he proved the presence of aniline and quinoline in coal-tar. A later investigation was on the metamorphoses of indigo, and in this he showed that hydrogen can be replaced by chlorine.

In 1845 Hofmann left Giessen, and became privatdocent in Bonn, where he lectured on Agricultural Chemistry. From Bonn he went to England to take charge of the new Royal College of Chemistry, an institution modeled after the laboratory which was so successful in Giessen. In 1853 he became professor of chemistry in the Royal School of Mines, still remaining at the head of the College of Chemistry. In 1864 Hofmann was invited to Bonn to build a university laboratory and to become its director. Before he could take charge of the new laboratory at Bonn, he was called to Berlin, in 1865, as Mitscherlich's successor, and there he remained until his death. For many years he was active in chemical work, though during the last few years of his life he was much less active than formerly. To a very remarkable degree he retained his interest in the progress of chemistry to the last, and it appears that at the time of his death he was engaged upon an investigation on the isonitriles. The last publication bearing his name is one entitled "Ueber polymeres Methylsenföl," which appeared in the number of the Berichte of March 28, 1892. At the end of the brief article he says: "I hope after the Easter vacation to communicate to the Society details concerning these compounds." There are few indeed who have kept their hands to the chemical plough for over fifty years!

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[1] Ante **13**, 497.

[2] Ibid. **13**, 579, note 2.

[3] This Journal **13**, 559.

There is no question that Hofmann exerted a powerful influence upon the chemists of the last half-century, and that his work contributed largely to the advance of the science. His researches on aniline and similar bases were extraordinarily fruitful from the point of view both of pure science and of chemical industry. They led to the present conception of the constitution of aniline, so far as its relation to ammonia is concerned, and formed an important part of the foundation of that which is called "modern chemistry." On the other hand, the dyestuff industry owes an enormous debt to him. In 1858 he obtained fuchsine by treating aniline with carbon tetra-chloride, and to the investigation of this compound he devoted many years. Among his other most important investigations should be mentioned those on guanidine, formic aldehyde, iso-nitriles, mustard-oils, the alkaloids, the phosphine bases, etc.

He has received abundant evidence of the esteem in which he was held by the chemical world as well as by the world at large. Honor after honor has been paid him, the culmination being reached in the celebration of his 70th birthday, April 8, 1888, and of the fiftieth anniversary of his doctorate, August 9th, 1891.[1]

I. R.

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[1] The writer of this notice is largely indebted to an article in the Chemiker-Zeitung (Vol. 16, No 38).

VOL. XIV. [MAY, 1892.] NO. 5.

AMERICAN

CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LXXIII.—ON THE PRODUCTS OBTAINED BY THE ACTION OF NITRIC ACID UPON BROMTRINITROPHENYLMALONIC ESTER.

BY C. LORING JACKSON AND W. B. BENTLEY.

Our attention was first called to this subject by the appearance of a vivid red color when common strong nitric acid was used to set free bromtrinitrophenylmalonic ester from its sodium salt, whereas no such color was observed if hydrochloric or sulphuric acid was used in place of nitric. Upon studying this action, we soon found that a new compound was formed, which could also be obtained from the free bromtrinitrophenylmalonic ester by treating it with hot nitric acid for a few minutes,[1] or for some hours in the cold; the free ester therefore acts with nitric acid less readily than its salt, for with that the color appeared immediately. The further study of this compound (which was obtained in colorless prisms) proved that its formula was $C_6HBr(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$; that is, that it had been formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the group NO_2. We have also obtained the following similar derivatives: from the bromdinitrophenylmalonic ester

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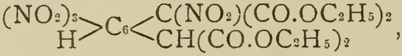
[1] A preliminary account of this substance forms part of a paper by G. D. Moore and one of us (This Journal **12**, 7). The statements made there are superseded by this paper.

$C_6H_2Br(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$, melting-point 111°, and from the trinitrophenylenedimalonic ester,



$$\begin{matrix}(NO_2)_3\\H\end{matrix}\!>C_6<\!\begin{matrix}C(NO_2)(CO.OC_2H_5)_2\\CH(CO.OC_2H_5)_2\end{matrix},$$

also melting at 111°, so that the reaction seems to be a general one. The position of the group NO_2 introduced by the action of nitric acid was determined by the study of the acidity of these compounds. In the bromtrinitrophenylmalonic ester $C_6HBr(NO_2)_3.CH(CO.OC_2H_5)_2$ there are only two atoms of hydrogen, one on the benzol ring, the other on the side-chain; if the first of these were replaced by the nitro group, the effect, if any, would be to increase the acidity of the compound; whereas, if the atom of hydrogen on the side-chain were replaced, the substance would cease to show acid properties, as the nitro group would have taken the place of the only atom of hydrogen which can be replaced by a metal. Upon studying the behavior of the new compound with alkaline reagents, we found that none of them affected it in aqueous solution, and that it was acted on only by sodic hydrate or ethylate in alcoholic solution, thus showing a marked contrast to the behavior of bromtrinitrophenylmalonic ester, which is acid enough to decompose sodic carbonate in aqueous solution. As just stated, sodic hydrate or ethylate does act upon our substance, but the red solution formed by the sodic ethylate was proved to contain sodic nitrite, and therefore the formation of the red salt was preceded by the removal of the group NO_2, which proves that this radicle has replaced the hydrogen of the side-chain, as represented in the formula given above. This result was confirmed by the study of the compound $C_6H_2Br(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$, which proved even less susceptible to the action of alkalies than the corresponding trinitro-compound. The replacement of the hydrogen in the malonic ester radicle is not at all strange, since Franchimont and Klobbie[1] have found that nitric acid converts malonic ester into nitromalonic ester.

To determine whether our substances were nitro-compounds, that is, with the radicle NO_2 attached to the side-chain by its nitrogen, or nitrites, that is, with the radicle attached by one of its atoms of oxygen, we considered in the first place the further action of nitric acid upon the compound $C_6HBr(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$, which converted it after warming for three hours into $C_6HBr(NO_2)_3.C.OH.(CO.OC_2H_5)_2$, that is, the bromtrinitrotartronic ester; the reaction seemed to run smoothly, and the yield was 40 per cent. of the theoretical. A similar change was produced by heat; when exposed to a temperature of 124°–126° the substance melted, turned blood-red, and gave off a great deal of gas, with a striking increase in volume at the same time.[1] A study of the gases showed that a part of the substance had undergone complete decomposition, as they contained bromine; the residue, however, furnished a considerable amount of the substituted tartronic ester mentioned above. The action therefore has a certain resemblance to the conversion of the nitrate of tartaric acid into tartronic acid. These easy conversions of the compound containing the group NO_2 into the corresponding tartronic ester can be best explained on the theory that this group is attached to the side-chain by oxygen, but cannot be considered as a strict proof of this point. Accordingly we have reduced with tin and hydrochloric acid the substance $C_6H_2Br(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$ (selected because it can be obtained more easily than the trinitro-compound), and have found that it yields ammonic chloride and a substance having the formula $C_6H_3.NH_2.(CH.OH.CO.NH)HCl$, that is, the chloride of amidoxyoxindol; there can be no doubt, therefore, that the group NO_2 is attached to the side-chain by one of its atoms of oxygen, and the substances are nitrites and not nitromalonic esters.

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[1] Ber. d. chem. Ges. **23**, Ref. 62 from Recueil trav. chim. **8**, 283. For a discussion of the effect of different radicles upon the action of nitric acid on fat substances, see Franchimont: Ber. d. chem. Ges. **20**, Ref. 689 from Recueil trav. chim. **6**, 224, and Ber. d. chem. Ges. **23**, Ref. 64 from Recueil trav. chim. **8**, 307.

One of the most striking properties of the nitrite of bromtrinitrophenylmalonic ester is its slight stability. As has been already stated, it decomposes rapidly, with change of color and evolution of gas, at 124°–126°, but it is not necessary to heat to this temperature to bring about the decomposition, as it also takes place slowly at 100°, and partially even at 70°. Boiling with alcohol decomposes the substance completely, and boiling water produces a similar but less complete change. The nitrites of the corresponding dinitro-compound and of the trinitrophenylenedimalonic ester are much more stable.

As has been stated above, the nitrite of bromtrinitrophenylmalonic ester, if warmed for three hours with strong nitric acid, or heated alone to its decomposition-point, yields a product in which the radicle of the nitrous acid has been replaced by hydroxyl, and which is therefore bromtrinitrophenyltartronic ester; this substance melts at 156°, and possesses marked acid properties. It is not necessary, however, to make it from the nitrite, as the bromtrinitrophenylmalonic ester is converted directly into it by warming for three hours with nitric acid. This therefore is a case of the direct oxidation of tertiary hydrogen to hydroxyl,[1] and, as we have succeeded in isolating the intermediate product, our work throws some light on the mechanism of the reaction, showing that it consists in the case of nitric acid of the formation of a nitrite, followed by its saponification to the hydroxyl compound.

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[1] These phenomena shown by our substance in melting, as well as many of its other properties, are very similar to those observed by Gabriel in the cases of the benzylidenephthalide dinitrite, Ber. d. chem. Ges. **18**, 1255, and the ethindiphthalide dinitrite, Ber. d. chem. Ges. **19**, 837, which confirms the view that our substance is a nitrite.

$C_6H(C_6H_5NH).(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$, the nitrite of anilidotrinitrophenylmalonic ester, was obtained by the action of aniline on the corresponding bromine compound; it forms red rhombohedra, which melt at 119°, decomposing at one degree higher, and shows marked acid properties, which must be due to the effect of the three nitro-groups upon the hydrogen attached to the nitrogen in the anilido-group, since, as has already been stated, the corresponding bromine compound forms no salts. This conclusion was confirmed by the study of the anilidotrinitrotoluol, which contains no other hydrogen capable of being replaced by a basic radicle, and yet formed the sodium salt $C_6.CH_3.H(C_6H_5.NNa).(NO_2)_3$. As was to be expected, however, this toluol compound was not so acid as the nitrite of anilidotrinitrophenylmalonic ester, which contains such a very negative radicle in place of the methyl.

The anilidotrinitrotartronic ester was also made from the corresponding bromine compound, and was obtained in two modifications: one, formed at higher temperatures, appeared in orange-red prisms melting at 143°, the other in rounded masses of yellow needles melting at about 122°. Both show the same percentage composition on analysis, and one is easily converted into the other; the yellow into the red by allowing the alcoholic solution to crystallise at about 60°, by heating the solid a little below its melting-point, or by boiling it with water; the red into the yellow by solution in glacial acetic acid and precipitation with water. Unfortunately we have not succeeded in determining the molecular

[1] Richard Meyer: Ann. Chem. (Liebig) **219**, 234; **220**, 1; J. Bredt: Ber. d. chem. Ges. **14**, 1780.

weights of these substances, as we have not yet found a solvent that gives satisfactory results with Raoult's method. The work on these substances will be continued in this laboratory, especially with a view to determining whether the nitrogen is the cause of the isomerism (if they are not polymers), but we may say now that this does not seem very probable to us on account of the striking resemblance in properties[1] between our two substances and the two forms of benzilorthocarbonic acid described by Graebe.[2]

The anilidotrinitrophenyltartronic ester forms salts with one atom, $C_6H(C_6H_5.NH).(NO_2)_3C.OM.(CO.OC_2H_5)_2$, or with two atoms of univalent basic radicles, $C_6H(C_6H_5.NM)(NO_2)_3C.OM.(CO.OC_2H_5)_2$. To our great surprise, the disodic salt was formed even when the ester was present in large excess. This tartronic ester is much more strongly acid than the anilidotrinitrophenylmalonic ester (melting-point 133°), a fact which confirms the formula assigned to it. We may add that we have failed in all our attempts to convert anilidotrinitrophenylmalonic ester into its nitrite, or the corresponding tartronic ester, by the action of nitric acid.

We have also tried without success to convert the bromdinitrophenylmalonic ester into dinitrophenylenedimalonic ester by the further action of sodium-malonic ester.

The remainder of the paper contains the experimental details of the work.

Preparation of Tribromtrinitrobenzol.

The experience gained in making tribromtrinitrobenzol for the work described in this paper has led us to introduce into the process given in previous papers[3] from this Laboratory some improvements, which are described in this section.

To the preparation of tribromaniline we have nothing to add, but in the conversion of it into tribrombenzol we have found it best to proceed as follows: 50 grams of dry tribromaniline were dissolved with the aid of heat in 300 cc. of alcohol containing 75 cc. of benzol to increase its solvent power, and 20 cc. of common strong sulphuric acid added to the hot solution from a pipette. If this formed a precipitate, it was dissolved by longer heating, more of the solvents being added if necessary. 20 grams of finely powdered sodic nitrite were then sifted into the hot liquid, as rapidly as the violence of the action would permit; after which the whole was heated until the effervescence had ceased, and, after standing over night, filtered, washed, and dried, when the product could be treated directly with nitric acid to make the tribromdinitrobenzol in the manner already described.[1] The yield of tribrombenzol was good, 42–44 grams from the 50 grams of tribromaniline. The filtrate and washings contained so little of the organic substance that it was not worth while to work them up.

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[1] It is a curious fact that even the melting-points are nearly the same.

[2] Ber. d. chem. Ges. **23**, 1344.

[3] This Journal **10**, 284; **12**, 9, 166.

In the conversion of this body into tribromtrinitrobenzol we have found the cause of the much larger yield obtained by Dr. Moore[2] than by Dr. Wing.[3] This does not depend so much on the larger proportion of fuming sulphuric acid used, as on the rapidity with which the boiling is carried on. To get the best yield we found it necessary to raise the mixture to the boiling-point as quickly as possible, and to keep it boiling violently during the whole of the three hours. Under these conditions the yields varied from 8 to 10 grams of tribromtrinitrobenzol from 20 grams of tribromdinitrobenzol, that is, 36 to 45 per cent. of the theoretical, if both the nitric and fuming sulphuric acids were of the best quality. To prove that this violent boiling was the cause of the large yields, in one experiment the mixture was allowed to stand in the cold for a week, and then kept barely at the boiling-point for seven hours, when it yielded only 18 per cent. of the tribromtrinitrobenzol.

The Nitrite of Bromtrinitrophenylmalonic Ester, $C_6HBr(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$.

This substance was prepared as follows: 3 grams of bromtrinitrophenylmalonic ester[4] were mixed with about 10 grams of nitric acid, specific gravity 1.38, and warmed in a dish for three minutes on the water-bath, when both the undissolved organic substance and the acid became intense blood-red; the mixture was then allowed to cool, the acid liquid poured off, and the solid residue warmed once more for two minutes with about the same volume of fresh acid. After this the acid was decanted off, and the solid crystalline product washed with water till free from nitric acid, which changed it from a deep blood-red to a pale reddish-white color. The purification of this substance gave us much trouble at first on account of its slight stability, since even the short warming necessary to dissolve it in alcohol was sufficient to decompose it partially, while longer heating with alcohol produced complete decomposition; but at last we obtained satisfactory results from the following method: The crude substance, after the thorough washing with water mentioned above, was dissolved in warm chloroform, in which it is freely soluble, but even with this solvent care must be taken to warm the mixture for as short a time as possible; it was advisable, therefore, to achieve the solution rather by the use of a larger quantity of chloroform than by using a smaller volume at a higher temperature. This chloroform solution was then diluted with about its own volume of common alcohol, when the substance gradually separated in well formed white prisms, and was obtained pure after two of these crystallisations. It must be dried *in vacuo*, as it decomposes on the water-bath; in fact, even the temperature of a steam radiator (about 70°) was sufficient to bring about a partial decomposition.

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[1] This Journal **12**, 166.
[2] Ibid. **12**, 9.
[3] Ibid. **10**, 285.
[4] Melting at 104° (This Journal **12**, 9.)

A small additional amount of this substance could be obtained from the red nitric acid mother-liquors formed in its preparation, either by adding water or by evaporating them to dryness; but this quantity is so small that it is not worth the amount of work necessary to free it from the red viscous impurity with which it is mixed, especially as the mother-liquors can be used to more advantage for the preparation of the bromtrinitrophenyltartronic ester made by the longer action of hot nitric acid on bromtrinitrophenylmalonic ester.[1]

The same substance was formed when the bromtrinitrophenylmalonic ester stood in the cold with nitric acid of specific gravity 1.38 for three days. At first there was no visible change, but after two hours the mixture began to show a red color, which increased in intensity to a deep blood-red. The product was purified in the way just described, but this method of making it is on the whole not so good as that at a temperature of 100°.

The ease with which the substance breaks up under the influence of heat rendered the combustion of it a matter of great difficulty, since we encountered at one time an almost explosive evolution of gas, and at another the formation of a partial vacuum in the tube. The latter we are inclined to ascribe to the sudden absorption by the plumbic chromate of the large quantity of bromine given off by the substance. We finally succeeded in getting good results by spreading out the weighed portion through the whole length of a long porcelain boat, and then applying the heat so gradually that a layer of not more than a few millimeters of it melted at any one time. Care was also taken that the temperature did not rise much above 115° until the whole of the substance had been melted, after which the combustion was finished in the usual way without trouble.

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[1] On one occasion the acid mother-liquors yielded by spontaneous evaporation large white prisms, which melted in the crude state at about 99°, and were apparently somewhat soluble in water; but, although we have tried in many ways, we have not succeeded in obtaining this substance a second time.

The analyses led to the following results:

I. 0.2157 gram substance gave on combustion 0.2514 gram CO_2 and 0.0496 gram H_2O.

II. 0.1978 gram substance gave 0.2310 gram CO_2 and 0.0428 gram H_2O.

III. 0.1978 gram substance gave 0.2324 gram CO_2 and 0.0430 gram H_2O.

IV. 0.2014 gram substance gave 20.6 cc. nitrogen at a temperature of 24° and a pressure of 772.6 mm.

V. 0.1890 gram substance gave 18.6 cc. nitrogen at a temperature of 19° and a pressure of 752.8 mm.

VI. 0.2101 gram substance gave by the method of Carius 0.0813 gram AgBr.

VII. 0.2078 gram substance gave 0.0792 gram AgBr.

VIII. 0.2054 gram substance gave 0.0776 gram AgBr.

	Found.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon	31.79	31.84	32.03	...	...	...	...	...
Hydrogen	2.56	2.40	2.42	...	...	...	...	...
Nitrogen	...	...	...	11.66	11.20	...	...	...
Bromine	...	...	...	...	...	16.47	16.22	16.08

These analytical results agree best with the percentages required by a substance formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the radicle NO_2, as is seen from the following table:

	Calculated for $C_6HBr.(NO_2)_3.C.NO_2.(CO_2C_2H_5)_2$.	Found. Mean.
Carbon	31.52	31.88
Hydrogen	2.22	2.46
Nitrogen	11.32	11.43
Bromine	16.16	16.26

Our reasons for the position assigned to the radicle NO_2 in this formula, and for supposing that it is not a nitro group ($-N\equiv O_2$), but a nitrite group ($-O-N=O$), have been already stated in the introduction to this paper. The yield is satisfactory on the whole; 5 grams of bromtrinitrophenylmalonic ester gave 3.26 grams of the substance,[1] instead of the 5.5 grams required by the calculation, that is, 59 per cent. of the theoretical yield.

Properties of the Nitrite of Bromtrinitrophenylmalonic Ester.—It occurs usually in short, thick, well-developed, glistening white prisms, with terminations consisting of two planes at both ends, which seem to indicate that the crystals belong to the monoclinic system. Less commonly the prisms are long and rather slender, with terminations similar to those of the shorter form. Its behavior when heated is very characteristic. If a tube containing some of it is dipped into an oil-bath at 124°–126°, the substance turns red round the sides, then deeper, and the action gradually runs through the mass, until after a second or two the whole is melted, forming a dark blood-red liquid, which occupies many times the volume of the original substance, and contains bubbles of gas. The action is evidently a decomposition, and can be produced at much lower temperatures, since if the tube containing the substance, instead of being dipped into the heated bath as described above, is gradually heated with the bath, the action takes place even below 120°. In fact, it can also be brought about by long-continued heating in the steam-bath, or partially even at 70°. It is evident, therefore, that the compound has no definite melting- or decomposition-point, but yet the temperature given at first (124°–126°) can be used as such in purifying the substance, since it is essentially constant, if care is taken always to heat the samples examined in the same way.

This decomposition seemed so interesting that we examined it more carefully. For this purpose a considerable quantity of the nitrite of bromtrinitrophenylmalonic ester was heated in a test-tube inserted in an air-bath, and the gaseous products of the reaction drawn through a solution of baric hydrate. At 103°–108° there was a quantity of red vapor given off, and a precipitate of baric carbonate formed in the tubes containing the baric hydrate solution. The red vapor was recognised by the smell as bromine, and this was confirmed by the precipitation of argentic bromide when argentic nitrate was added to the acidified filtrate from the baric carbonate. On the other hand, we could not detect a trace of nitrate or nitrite with ferrous sulphate and sulphuric acid. After the substance had been heated to 103°–108° for three hours, the temperature was raised to 125° for two hours and a half, but the additional loss at this higher temperature was very small. We intended originally to determine quantitatively the amounts of the various products, but abandoned this idea when we found that the loss was not constant, three experiments giving 25 per cent., 30 per cent., and 21 per cent., respectively. The appearance of the bromine, too, shows that there has been a complete decomposition of a part of the substance, and therefore the volatile products are of so little interest that we did not care to spend the time necessary for the identification of the others, which must have been formed in addition to the bromine and carbonic dioxide. On the other hand, we were much interested in the non-volatile product of the reaction left in the test-tube as a fused, rather viscous mass of a brownish red color, in which crystals were imbedded. It was purified by washing several times with alcohol, which removed much of the viscous portions; then the residue was crystallised, first from dilute, and finally from common alcohol, and when pure showed the melting-point 156° and the crystalline form of the bromtrinitrophenyltartronic ester described later in this paper. The action of heat on our nitrite, therefore, is similar to the well-known conversion of the so-called nitrotartaric acid into tartronic acid.

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[1] In addition to this amount 0.7 gram of bromtrinitrophenyltartronic ester was obtained from the mother-liquors.

The nitrite of bromtrinitrophenylmalonic ester is almost insoluble in cold water, perhaps a little more soluble in boiling water; but if the substance was boiled for some time with water, the crystals were converted superficially into a dark red, oily substance, and the water gave a slight test for bromine; this decomposition seemed to be due, however, only to the heat (see above), not to the presence of the water. It is slightly soluble in cold, more freely in hot ethyl alcohol, but this solution is easily decomposed by heat, since boiling for fifteen minutes converts the substance completely into a brownish red, viscous product, resembling half-dried varnish, from which nothing definite could be isolated, and even a very short heating with alcohol is sufficient to form some of this viscous body. Its solubility in methyl alcohol resembles that in ethyl alcohol; it is freely soluble in chloroform or acetone; soluble in benzol or glacial acetic acid; slightly soluble in carbonic disulphide; very slightly in ether, and essentially insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol described above. Strong sulphuric acid seems to have no action on it in the cold, or if heated, until the substance decomposes, when it dissolves, forming a reddish solution; strong hydrochloric acid has no action on it, either hot or cold, as long as the substance does not decompose; strong nitric acid has little or no action on it in the cold, even when allowed to stand with it for some weeks; when heated to 100° it converts it gradually into the bromtrinitrophenyltartronic ester, as is described in detail later in this paper under the preparation of that substance.

Ammonic hydrate acts on it little, if at all, even when the action is assisted by the addition of alcohol; sodic hydrate in aqueous solution has no action, but if alcohol is added the crystals begin to dissolve slowly, imparting a red color to the liquid, but only a partial solution is effected in the cold. From this observation we inferred that no salt was formed until the nitrite was decomposed, and to test the accuracy of this inference we treated some of the nitrite with an alcoholic solution of sodic ethylate, which gave at once a dark blood-red coloration; but even here only a part, and that not the larger part, of the crystals of the nitrite was dissolved; the red solution poured off from the unaltered crystals gave a good test for a nitrite with starch paste, potassic iodide, and dilute sulphuric acid, with ferrous sulphate and sulphuric acid, and by Liebermann's reaction, so that there can be no doubt that sodic nitrite was formed in the experiment. This proves the correctness of our inference that the substance melting at 124°–126° cannot form salts; and the blood-red salt observed must have been derived from the decomposition-product left after the removal of the group NO_2 from our substance. It may be added that acid or neutral sodic carbonate has no action on the nitrite in aqueous solution, and very little, if any, in presence of alcohol.

Nitrite of Anilidotrinitrophenylmalonic Ester,
$C_6H(C_6H_5NH).(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$.

Aniline acts with great violence on the nitrite of bromtrinitrophenylmalonic ester. If the substances are mixed at ordinary temperatures, the action is almost explosive, a good part of the mixture is thrown out of the beaker, and the product seems to be principally carbon. If the mixture is kept cool by immersing the beaker in water, the action goes more mildly, but the product is still very black and impure. We therefore carried on the reaction in ethereal solution with the best results as follows: 1 gram of the nitrite of bromtrinitrophenylmalonic ester was mixed with a small quantity of ether, and, disregarding the fact that a portion of the crystals had not dissolved, a slight excess of aniline was added; the ether at once turned red, and the undissolved crystals of the nitrite were taken up, while aniline bromide was deposited in their place. At the end of a few minutes the reaction was complete, and, after washing out the aniline and aniline bromide with water containing a little hydrochloric acid, the ether was allowed to evaporate, when it left a vivid red mass, which was purified by dissolving it in hot chloroform, avoiding long heating, and then adding alcohol until the crystals began to separate, as it had been found that this substance, like the corresponding bromine-compound, was decomposed by heating with alcohol. After the substance showed the constant melting-point 119° it was dried *in vacuo* for analysis.

The combustion of this substance was even more difficult than that of the bromine-compound, as it decomposed with almost explosive violence at a temperature a few degrees above its melting-point, and did not begin to decompose at all at lower temperatures. We were unable therefore to burn it in an open tube, but at last got satisfactory results by using a closed tube, mixing it with a long layer of plumbic chromate and applying the heat very gradually. Its analyses led to the following results:

I. 0.1542 gram substance gave on combustion 0.2538 gram CO_2 and 0.0678 gram H_2O.

II. 0.1494 gram substance gave 18.9 cc. nitrogen at a temperature of 24.3° and a pressure of 752.3 mm.

	Calculated for $C_6H(C_6H_5NH).(NO_2)_3.C.NO_2.(CO_2C_2H_5)_2$.	Found. I.	II.
Carbon	44.97	44.88	...
Hydrogen	3.35	4.88	...
Nitrogen	13.80	...	14.02

In spite of the unsatisfactory number for the hydrogen, these results prove that the substance has the formula which we have assigned to it. The yield was good, 0.9 gram of the nitrite of the bromtrinitrophenylmalonic ester giving 0.7 gram of the anilido-compound, instead of the 0.92 gram required by the theory, that is, 76 per cent.

Properties.—The nitrite of the anilidotrinitrophenylmalonic ester is a very beautiful substance, crystallising in rhombohedra often two millimeters long and one millimeter thick, with a very acute angle, which is frequently, but not always, truncated by a basal plane. The color of the crystals by reflected light is a rich full red, somewhat darker than that of chromic anhydride; by transmitted light, orange-red. It melts at 119°, turning black and giving off a few bubbles of gas, if the temperature has not risen above this point; but at 120° it decomposes with such violence that frequently a good part of the substance is thrown out of the capillary melting-tube. It is essentially insoluble in cold water, and its solubility does not seem to be increased by heat; very slightly soluble in cold ethyl alcohol, more soluble in hot, but still not freely, the hot solution seems to undergo partial decomposition; more soluble in methyl alcohol, whether cold or hot, than in ethyl alcohol, but not freely even in this; very freely soluble in chloroform; freely in benzol or acetone; soluble in glacial acetic acid; slightly in ether or carbonic disulphide; insoluble in ligroine. The best solvent for it is a mixture of chloroform and alcohol. Strong sulphuric acid seems not to act on it in the cold, but when heated with it the substance decomposes, and then dissolves with a blackish color; strong nitric acid does not act on it in the cold, but when hot dissolves it with a yellow color; strong hydrochloric acid has no action on it, whether cold or hot.

The nitrite of anilidotrinitrophenylmalonic ester showed marked acid properties. Acid sodic carbonate in aqueous solution had no action with it, but, if assisted with alcohol, gave a red solution; potassic carbonate behaved in the same way; sodic hydrate turned the crystals black, forming at the same time a brownish solution, which on addition of alcohol became deeper and blackish red, turning in time to blackish brown; ammonic hydrate in aqueous solution gave a red color, but the action was not complete until alcohol was added, when a very dark red solution was formed. The nitrite of anilidotrinitrophenylmalonic ester therefore shows much more acid properties than the corresponding bromine-compound, which is indifferent to all these reagents except sodic hydrate in presence of alcohol, and this fact puzzled us at first, until we decided that the hydrogen attached to the nitrogen in the anilido radicle (C_6H_5NH) might be rendered acid by the presence of the three nitro groups. That this is the correct explanation of the phenomenon we have proved by preparing and analysing the sodium salt of anilidotrinitrotoluol, which contains no atom of hydrogen that could be replaced by sodium except the one attached to the nitrogen of the aniline radicle. The description of this work will be found in the following section.

An attempt to analyse the sodium salt of the nitrite of anilidotrinitrophenylmalonic ester gave no satisfactory result, owing undoubtedly to the partial formation of sodic nitrite from the organic nitrite by the action of the sodic hydrate used in making the salt.

Sodium Salt of Anilidotrinitrotoluol,
$C_6.CH_3.H.(C_6H_5NNa).(NO_2)_3$.

To prepare this salt, 1 gram of anilidotrinitrotoluol[1] (melting-point 151°) was dissolved in alcohol, and mixed with an alcoholic solution of 0.09 gram of sodic hydrate, that is, over 0.03 gram less than the amount required to convert the gram of substance into its salt; a little ether was then added, and the solution of the salt evaporated rapidly to dryness in a narrow beaker sunk throughout its whole length in the steam-bath. During the evaporation there was an odor of phenyl isocyanide. The dry mass was washed thoroughly with benzol to remove the excess of anilidotrinitrotoluol, the residue dried at 100°, and analysed. As the salt explodes when heated with strong sulphuric acid, it should be dissolved in water, treated with dilute sulphuric acid, filtered, and the filtrate evaporated to dryness and converted into neutral sodic sulphate.

0.7876 gram salt gave 0.1662 gram Na_2SO_4.

	Calculated for $C_6.CH_3.H.(C_6H_5NNa).(NO_2)_3$.	Found
Sodium	6.76	6.84

The salt prepared as described above forms a maroon-black powder, which explodes gently when heated alone, or with strong sulphuric acid, forming in the latter case a very loose, spongy, blackish mass. It is soluble in alcohol with a yellowish brown color like that of ferric chloride; insoluble in ether or benzol; water decomposes the salt almost completely, forming a yellow precipitate and a pale brown solution, which is strongly alkaline. The action of the anilidotrinitrotoluol with alkaline reagents was also studied, and, as was to be expected, no action was obtained with acid or neutral carbonate of sodium, or ammonic hydrate in aqueous solutions; but if the action was assisted by the presence of alcohol, each of these reagents gave a barely perceptible reddish coloration, so slight in the case of ammonic hydrate that we were doubtful whether there had been any action; sodic hydrate in aqueous solution gave a slight yellow coloration, which, on the addition of alcohol, was at once converted into a very dark blood-red. The acid character of the anilidotrinitrotoluol therefore is much less marked than that of the nitrite of anilidotrinitrophenylmalonic ester, and as the position of the anilido group with regard to the nitro groups is the same in both compounds, we must ascribe this to the presence of the nitrite of the malonic-ester radicle $C.NO_2.(CO.OC_2H_5)_2$, with its large amount of oxygen in place of the indifferent methyl contained in the toluol.

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[1] This Journal **12**, 6.

Bromtrinitrophenyltartronic Ester, $C_6HBr.(NO_2)_3.C.OH.(CO.OC_2H_5)_2$.

If the nitrite of bromtrinitrophenylmalonic ester, or the ester itself, was heated for some time with nitric acid, it was converted into the corresponding tartronic ester, which we found it convenient to prepare as follows: 1 gram of bromtrinitrophenylmalonic ester was mixed with about 10 cc. of nitric acid of specific gravity 1.38, and heated on the water-bath for three hours in a dish covered with a watch-glass, fresh nitric acid being added when necessary to replace that lost by evaporation. At the end of this time the substance was found to be completely dissolved in the small quantity of hot nitric acid left, but upon cooling colorless crystals separated, which, after washing with water, were essentially the pure substance, one recrystallisation from alcohol being all that was needed to make them melt at 156°, the constant melting-point of this compound. If, as was usually the case, the bromtrinitrophenylmalonic ester was contaminated with acetylenetetracarbonic ester, a yellowish oil was also formed, which, however, remained dissolved in the nitric acid mother-liquor. The amount of the substituted tartronic ester in this mother-liquor was so small that it did not pay for the working up.

The bromtrinitrophenyltartronic ester can also be made from the nitrite of the corresponding malonic ester, but this method has no advantage over the preparation direct from the malonic ester described above, except in the case of the nitric acid mother-liquors from making the nitrite, which yield on longer heating with nitric acid a small amount of the tartronic ester, and this is worth saving on account of the tedious and costly preparation of the mother-substance.

The substance dried *in vacuo* was analysed with the following results:

I. 0.1951 gram substance gave on combustion 0.2380 gram CO_2 and 0.0584 gram H_2O.

II. 0.2049 gram substance gave 16.2 cc. nitrogen at a temperature of 17.5° and a pressure of 763.7 mm.

III. 0.2044 gram substance gave according to the method of Carius 0.0836 gram AgBr.

IV. 0.2272 gram substance gave 0.0930 gram AgBr.

	Calculated for $C_6HBr.(NO_2)_3.C.OH.(CO_2C_2H_5)_2$.	Found.			
		I.	II.	III.	IV.
Carbon	33·47	33·28	...	...	...
Hydrogen	2.58	3·33	...	...	...
Nitrogen	9.02	...	9.20	...	...
Bromine	17.17	...	...	17.41	17.42

Our reasons for considering this a tartronic ester rather than a phenol have been given already in the introduction to this paper. The yield is satisfactory, considering the amount of loss to be expected from such a method of preparation: 1 gram of bromtrinitrophenylmalonic ester gave 0.4 gram of the substance, or about 40 per cent. of the theoretical yield.

Properties.—The bromtrinitrophenyltartronic ester crystallises from alcohol in long white prisms, terminated by planes at a very obtuse angle to each other, so that the ends look almost but not quite square. These crystals are often arranged in radiating groups, and in that case are generally much more slender than when occurring in isolated prisms. It is deposited from its solution in hot nitric acid in rather sharp slender needles. It melts at 156°, and is nearly but not quite insoluble in water, whether hot or cold; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; freely soluble in benzol, glacial acetic acid, or acetone; soluble in ether, and somewhat more so in chloroform; nearly insoluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is hot alcohol. Strong sulphuric acid has no action upon it in the cold, but if hot dissolves it with difficulty with a reddish brown color; strong hydrochloric acid has no action on it, hot or cold, in open vessels, but decomposes it if the two substances are heated together in a sealed tube; nothing could be obtained from the products, however, except a mass like a dry varnish, which we did not succeed in bringing into a state fit for analysis. An exactly similar result was obtained in an attempt to saponify it with sulphuric acid of specific gravity 1.44. Strong nitric acid has no action on it at first, whether cold or hot, but if heated with it for some time seems to destroy it completely, and a similar result was obtained upon boiling it with bromine and water, as in both these cases we could not succeed in isolating any organic oxidation product.

Acid sodic carbonate in aqueous solution had no action on bromtrinitrophenyltartronic ester, but on the addition of alcohol a pale red color appeared, which became more marked on standing; potassic carbonate also did not affect it in aqueous solution, but gave a strong dark red solution on addition of alcohol; aqueous sodic hydrate turned the crystals brown, and dissolved some of them with a brownish color; on the addition of alcohol all the substance went into solution with a dark red color; ammonic hydrate gave a red solution, but the action was not complete until alcohol was added, when the solution became very dark red. The bromtrinitrophenyltartronic ester therefore showed the strong acid character which we should expect, but no attempt was made to analyse its salts, as it was found that the bromine atom was removed by alkaline solutions with great ease, sodic bromide being formed when it was treated with sodic ethylate, even in the cold.

Anilidotrinitrophenyltartronic Ester,
$C_6H.(C_6H_5NH).(NO_2)_3.C.OH.(CO.OC_2H_5)_2$.

This substance was made by adding an excess of aniline to solid bromtrinitrophenyltartronic ester; the reaction ran smoothly with a slight evolution of heat, and was complete after the mixture had been allowed to stand for a few minutes, when the aniline bromide and excess of aniline were removed by washing with very dilute hydrochloric acid, and the bright yellow residue purified by crystallisation from alcohol. At first rounded masses of radiating needles looking like little balls of fat of a bright yellow color were obtained, but as the crystallisation continued, orange-red prisms began to appear, and increased in quantity until after several recrystallisations the greater part of the substance had been converted into this form. This behavior during crystallisation suggested to us that the substance probably occurred in two modifications, which was proved to be the case by the determination of the melting-points of the two sorts of crystals, the yellow, after thorough purification, melting at about 122°, the red at 143°. As the substance passes from one form to the other with great ease, many experiments were necessary in order to find methods for obtaining each in a state of purity.

Red Modification of Anilidotrinitrophenyltartronic Ester.

To obtain this form from the crude product of the reaction it was crystallised several times from alcohol, until a mixture of the two forms rich in red had been obtained, and then a strong alcoholic solution of the mixed crystals was allowed to evaporate slowly at temperatures from 50° to 70°. The product thus obtained, which showed no sign of the yellow form, was dried at 100°, and analysed with the following results:

I. 0.1792 gram substance gave on combustion 0.3114 gram CO_2 and 0.0694 gram H_2O.

II. 0.2016 gram substance gave on combustion 0.3534 gram CO_2 and 0.0809 gram H_2O.

III. 0.1938 gram substance gave 19.9 cc. nitrogen at a temperature of 22° and a pressure of 767.7 mm.

	Calculated for		Found.	
	$C_6H.(C_6H_5NH).(NO_2)_3.C.OH.(CO_2C_2H_5)_2$.	I.	II.	III.
Carbon	47.69	47.40	47.80	...
Hydrogen	3.77	4.30	4.46	...
Nitrogen	11.71	...	...	11.76

The air-dried red crystals lost only 0.19 per cent. when dried at 100°, and therefore were free from water or alcohol of crystallisation.

Properties.—The red form of anilidotrinitrophenyltartronic ester crystallises in well formed prisms, often half a centimeter long, with at each end a pyramidal termination consisting of four planes. It has an orange-red color like that of potassic dichromate, and melts at 143°; is essentially insoluble in cold water, very slightly soluble in boiling water, forming a pale yellowish solution; soluble in cold alcohol, rather freely in hot. This solution if allowed to evaporate at temperatures from 50° to 70° deposits crystals of the red modification, as has been already stated; but if allowed to evaporate at ordinary temperatures, a mixture of red and yellow crystals is usually obtained, although occasionally only red crystals are formed under these conditions. The red modification is more soluble in methyl than ethyl alcohol; very freely in acetone. Both these solutions deposit some yellow crystals. Soluble in ether or chloroform; slightly soluble in cold benzol, freely in hot. The solution in benzol or chloroform deposits the substance in a viscous state. It is slightly soluble in cold glacial acetic acid, more soluble in hot; from this solution it is precipitated by the addition of water, usually in the yellow form, although once or twice we thought we obtained the red modification; very slightly soluble in carbonic disulphide; insoluble in ligroine. Strong sulphuric acid when cold has no action on it, but dissolves it with a brownish yellow color when hot; strong nitric acid dissolves it partially when cold with a yellow color, and the action is increased by heating; cold hydrochloric acid has no action on it, but dissolves it very slightly when hot.

Yellow Modification of Anilidotrinitrophenyltartronic Ester.

This substance was most conveniently obtained from the mixture of the two forms after it had been purified by several crystallisations from alcohol, by dissolving it in warm glacial acetic acid, and, after allowing the solution to stand for some hours, precipitating the solid matter by the addition of water. The yellow powder thus obtained was dried at ordinary temperatures over sulphuric acid, and anlysed with the following results:

I. 0.1879 gram substance gave on combustion 0.3284 gram CO_2 and 0.0726 gram H_2O.

II. 0.1924 gram substance gave 20.5 cc. nitrogen at a temperature of 25° and a pressure of 769.7 mm.

	Calculated for $C_6H.(C_6H_5NH).(NO_2)_3.C.OH.(CO_2C_2H_5)_2$.	Found. I.	II.
Carbon	47.69	47.66	...
Hydrogen	3.77	4.29	...
Nitrogen	11.71	...	12.05

The substance dried over sulphuric acid lost no weight when heated to 100°, showing that it contains neither water nor alcohol of crystallisation.

Properties.—The yellow form crystallises in very fine needles united into spherical groups like those of wavellite, looking frequently like little balls of fat, and has a full yellow color like that of potassic chromate. It is hard to determine the melting-point with accuracy, because this form is quickly changed into the red modification, at least in part, when heated to a few degrees below that temperature; it is necessary therefore to heat the bath up to the melting-point before immersing the capillary tube containing the substance; under these conditions it melts, and then changes to the red form, and solidifies again, after which it does not melt until about 140°. The melting-point we ascribe to this substance is 122°, but we are not sure that this is accurate to one degree. This change from yellow to red can also be brought about slowly by heating at 100°, by boiling the yellow form with water for some time, or, most conveniently, by crystallisation from alcohol at temperatures from 50° to 70°. In its solubility in the different solvents the yellow form does not differ much from the red, but seems in general to be more soluble.

We have made many attempts to determine the molecular weights of the two modifications by the method of Raoult, but have not as yet succeeded in finding any solvent which gives satisfactory results. Acetic acid, owing to its conversion of the red into the yellow form, could at best give results only for the latter, but a number of determinations showed us that it was of no use even for this purpose, as results were obtained varying from 295 to 345 (the theoretical molecular weight is 478), therefore showing that some reaction (probably the formation of an acetoxymalonic ester) had taken place between the acetic acid and the ester. An experiment with phenol gave an excellent result with the red form, 477 instead of 478; but with the yellow only 307 was obtained, indicating a chemical action similar to that observed with acetic acid, and we are not inclined to accept any result with phenol, however excellent it may appear, as with a substance which is so easily affected by solution as this there can be no certainty that it has remained in the same modification, unless it can be recovered directly from the solution used, and this we have found no means of doing in the case of phenol. Benzol gives such uncertain results with substances containing a hydroxyl group,[1] that we did not think it worth while to try it. We have hopes that naphthaline[1] may give the desired result for the red form; this will be tried in this laboratory, and a further attempt made to find a satisfactory solvent for the yellow modification; but as the departure of one of us from Cambridge makes it necessary to postpone further work in this direction until next year, we have thought it best to publish at once our present results, which have already reached a certain completeness.

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[1] Ber. d. chem. Ges. **21**, 707.

Salts of Anilidotrinitrotartronic Ester.

The anilidotrinitrotartronic ester has well marked acid properties. An aqueous solution of acid sodic carbonate has essentially no action on it, but if alcohol is added there is a slight but distinct action indicated by the change of color; potassic carbonate gives in aqueous solution a slight red color, which becomes a strong red if alcohol is added; sodic hydrate in aqueous solution gives a very dark red, apparently converting the substance completely into its salt; ammonic hydrate also gives a strong red color, which is intensified on the addition of alcohol. Some of the alkaline salts were studied more carefully with the following results:

Monopotassium Salt, $C_6H.(C_6H_5NH).(NO_2)_3.C.OK.(CO.OC_2H_5)_2$.

This salt was made by adding 20 cc. of absolute alcohol to 0.5 gram of the ester, and then a large excess of pure potassic carbonate; carbonic dioxide was given off, the solution became very dark red, and after digesting the substances for eight to ten minutes with the occasional aid of a little heat, the dark brown solution was filtered from the excess of potassic carbonate, evaporated to dryness in a beaker sunk throughout its whole length in the steam-bath, and analysed with the following results:

I. 0.3458 gram salt, heated with strong sulphuric acid, gave 0.0548 gram K_2SO_4.

II. 0.3748 gram salt gave 0.0696 gram K_2SO_4.

	Calculated for $C_6H.(C_6H_5NH).(NO_2)_3.C.OK.(CO_2C_2H_5)_2$.	Found.	
		I.	II.
Potassium	7.58	7.11	8.34

The absolute alcohol used in the second analysis had not been freshly prepared, and the slight excess of potassium can be accounted for by the assumption that it had absorbed a little water.

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[1] Ber. d. chem. Ges. **22**, Ref. 128.

Properties.—The acid potassic anilidotrinitrophenyltartronic ester, when prepared by the method described above, forms a brownish-black amorphous solid, freely soluble in water or alcohol, slightly soluble in ether, and insoluble in benzol. The solutions have a dark brown color.

Disodium Salt, $C_6H.(C_6H_5NNa).(NO_2)_3.C.ONa.(CO.OC_2H_5)_2$.

This salt seemed to be formed, to our great surprise, by the action of an alcoholic solution of sodic hydrate on an excess of the anilidotrinitrophenyltartronic ester. To prepare it, about 0.7 gram of the ester was mixed with a little alcohol, and somewhat less than the amount of sodic hydrate (also in alcoholic solution) necessary to form a mono-sodium salt; a little ether was then added to the dark red solution, which was evaporated rapidly to dryness, the small beaker containing it being sunk throughout its length in the steam-bath. After this the excess of unaltered ester was extracted with benzol, and the salt dried at 100°, and analysed with the following results:

I. 0.2596 gram salt gave after evaporation and ignition with sulphuric acid, 0.0672 gram Na_2SO_4.

II. 0.2848 gram salt gave 0.0698 gram Na_2SO_4.

	Calculated for $C_6H.(C_6H_5NNa).(NO_2)_3.C.ONa.(CO_2C_2H_5)_2$.	Found.	
		I.	II.
Sodium	8.81	8.39	7.94

These results agree with the percentage corresponding to the formula as nearly as can be expected, when it is remembered that the salt was not crystallised, or purified in any other way; but still we cannot feel that they do more than make it highly probable that this is the composition of the salt, as it is certainly strange that a neutral salt should have been formed when such an excess of the acid substance was present, and we had no means of proving that the substance analysed was a pure salt rather than a mixture; in fact, we observed a slight smell of phenyl isocyanide during its preparation, indicating a deep decomposition of part of it, —only a very small part, however, if we may judge from the smell.

Properties.—The salt prepared as described above formed a dark reddish brown to black amorphous mass, soluble in water or alcohol; slightly soluble in ether; insoluble in benzol. Its solutions have a brownish red color.

The behavior of a solution of the ammonium salt of anilidotrinitrophenyltartronic ester, made by adding ammonic hydrate to an excess of the ester, although it smelt strongly of ammonia, was tested with various reagents and gave the following characteristic precipitates:—

With a *zinc salt*, orange-brown.
With a *manganese salt*, brown.
With a *cadmium salt*, reddish brown.
With a *copper salt*, yellowish brown.
With a *lead*, *mercuric* or *silver salt*, reddish brown.

The fact that the ammonium salt gives no precipitate with salts of magnesium, calcium, strontium or barium, is also highly characteristic.

Although, as has been already stated, no definite results were obtained from our attempts to oxidise or saponify the bromtrinitrophenyltartronic ester, we thought that perhaps the anilido-compound might behave better, and accordingly the following experiments were made, in the hope (unfortunately not realised) of decomposing the anilidotrinitrophenyltartronic ester into substances which would confirm our inferences in regard to its nature. The substance was allowed to stand in the cold with an aqueous solution of potassic permanganate, but, although a considerable part of it disappeared, no organic oxidation product could be detected. In the hope of saponifying the ester, we added to it an excess of sodic hydrate dissolved in water, and allowed the reddish brown solution thus formed to stand in a corked flask at ordinary temperatures for some weeks. During this standing a strong odor of phenyl isocyanide was developed, and, if the amount of ester was small, the color changed to yellow; if, on the other hand, the quantity was large, it retained its dark brown color; at the end of the experiment, nothing was obtained except a brown precipitate of most unpromising appearance, formed by adding an acid to the solution, and the phenyl isocyanide already mentioned as recognised by its smell. As the formation of this substance would necessitate a complete destruction of the benzol ring which carried the nitro groups and malonic-ester radicle, we did not think it worth while to repeat the experiment.

This formation of an isocyanide from the destruction of a benzol ring containing nitro groups by means of an aqueous solution of sodic hydrate recalls the work of Post and Hübner,[1] who found that ordinary dinitrobenzol when boiled with a solution of sodic or potassic hydrate was decomposed with formation of a cyanide, quickly if the solution was strong, slowly if it was dilute. They also found that picric acid behaved in the same way, thus confirming the earlier observation of Wöhler.[1]

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[1] Ber. d. chem. Ges. 5, 408.

Anilidotrinitrophenylmalonic Ester, $C_6H.(C_6H_5NH).(NO_2)_3.CH(CO.OC_2H_5)_2$.

This substance was made to see whether it would be possible by treatment with nitric acid to convert it directly into either its nitrite or the anilidotartronic ester described above. It was found, however, that standing for several days at ordinary temperatures with strong nitric acid produced complete decomposition of part of the substance, the only product insoluble in the acid being unaltered anilidotrinitrophenylmalonic ester; and that upon heating it on the steam-bath with nitric acid for three hours in the hope of making the anilidotrinitrophenyltartronic ester, the substance was destroyed completely, oxalic acid being the only product which we could find. It seems therefore that the less acid anilido-compound cannot be converted into the nitrite or tartronic ester. But although these attempts to oxidise the substance have failed, we add the description of the anilidotrinitrophenylmalonic ester, which has not been prepared heretofore.

It is easily made by adding an excess of aniline to solid bromtrinitrophenylmalonic ester. The reaction ran smoothly in the cold with slight evolution of heat, and the product was purified by washing with very dilute hydrochloric acid to remove the excess of aniline and the aniline bromide, and crystallisation from alcohol until it showed the constant melting-point 133°, when, after drying at 100°, it was analysed with the following result:

0.1866 gram substance gave 20.2 cc. nitrogen at a temperature of 25.5° and a pressure of 764.3 mm.

	Calculated for $C_6H.(C_6H_5NH).(NO_2)_3.CH(CO_2C_2H_5)_2$.	Found.
Nitrogen	12.13	12.12

Properties.—The anilidotrinitrophenylmalonic ester crystallises in long, slender, sharp needles arranged in radiating bunches. It has a full yellow color, and melts at 133°. It is very slightly, if at all, soluble in cold water, more soluble in hot, as shown by the faint yellow color of the solution; freely soluble in hot alcohol, less so in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in chloroform; freely in benzol or acetone; soluble in ether, or glacial acetic acid; slightly in carbonic disulphide; insoluble in ligroine. Boiling alcohol is the best solvent for it. Strong sulphuric acid or nitric acid dissolves it slightly in the cold with a yellow color; the solubility is somewhat increased by heating; strong hydrochloric acid acts on it only very slightly, cold or hot. An aqueous solution of acid sodic carbonate has no action upon it, but there is a barely perceptible change of color if alcohol is added; aqueous potassic carbonate gives little if any action, but on the addition of alcohol a brown solution is formed; the action, however, seems to be incomplete; aqueous sodic hydrate turns the crystals dark and brown, the solution becoming yellow; the addition of alcohol seems to convert the substance completely into the sodium salt; aqueous ammonic hydrate gives a barely perceptible yellow color, which is not increased by the addition of a little alcohol, but a large amount gives a dark brown solution.

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[1] Ann. der Phys. Pogg. **13**, 488.

A solution of the sodium salt of anilidotrinitrophenylmalonic ester, made by adding a drop of sodic hydrate to an excess of the ester moistened with alcohol and then diluting largely with water, gave characteristic precipitates with the following reagents:

With a *calcium salt*, a heavy reddish brown precipitate.

With a *strontium salt*, a slighter precipitate.

With a *barium salt*, a very faint precipitate.

A *magnesium salt* gives a reddish brown precipitate, as heavy as that obtained with the calcium salt.

With a *manganese salt*, reddish brown flocks.

With a *zinc salt*, yellowish brown.

With a *cadmium salt*, orange-yellow.

With a *copper salt*, yellowish brown.

With a *lead salt*, reddish brown.

With a *silver salt*, dark reddish brown.

Its most striking property is that the barium salt is the most, the calcium salt the least, soluble of its salts with metals of the second group, and in this respect it resembles its mother-substance, the bromtrinitrophenylmalonic ester,[1] the corresponding acetacetic ester,[2] and the orthonitrobenzoylmalonic ester of Bischoff.[3]

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[1] This Journal **12**, 12.

[2] Ibid. **12**, 172.

[3] Ann. Chem. (Liebig) **251**, 362.

Nitrite of Trinitrophenylenedimalonic Ester,
$C_6H.(NO_2)_3.CH(CO.OC_2H_5)_2.C.NO_2.(CO.OC_2H_5)_2$.

After we had studied the action of nitric acid on the bromtrinitrophenylmalonic ester, it seemed of interest to determine whether the dimalonic-compound acted in the same way, and accordingly we proceeded as follows: A small quantity of the trinitrophenylenedimalonic ester[1] (melting-point 123°) was covered with nitric acid of specific gravity 1.38 and warmed in a dish on the steam-bath for two minutes; the solid turned dark yellow, and melted to a drop of oil. The acid was then allowed to cool, poured off, and replaced by the same quantity of fresh acid, when it was warmed as before for three minutes, making five in all. Upon standing, the oily product solidified to a mass of crystals, which were washed thoroughly with water, and at first recrystallised from alcohol; but as in each crystallisation a small quantity of yellow oil was formed, we feared a partial decomposition, and resorted to the method which had given excellent results in the purification of the nitrite of bromtrinitrophenylmalonic ester, that is, dissolving the substance with very little heat in chloroform, and then adding enough alcohol to start the separation of crystals; in this way a pure substance melting at 111° was obtained without difficulty, which was dried at about 70° and analysed with the following results:

I. 0.1960 gram substance gave on combustion 0.3012 gram CO_2 and 0.0714 gram H_2O.

II. 0.1926 gram substance gave 16.7 cc. nitrogen at a temperature of 23° and a pressure of 771 mm.

	Calculated for	Found.	
	$C_6H.(NO_2)_3.CH(CO_2C_2H_5)_2.C.NO_2.(CO^2C_2H_5)_2$.	I.	II.
Carbon	41.81	41.91	...
Hydrogen	3.83	4.05	...
Nitrogen	9.76	...	9.93

The substance is therefore the mononitrite of trinitrophenylenedimalonic ester.

Properties.—The substance crystallises in rather thick plates with parallel sides terminated at each end by two planes at an acute angle to each other, these acute angles being usually, but not always, truncated by planes at right angles to the parallel sides. The crystals are often much twinned and grouped into very irregular forms. It has a lemon yellow color, and melts without decomposition at 111°. It is very slightly soluble in boiling water, giving a pale yellow solution, essentially insoluble in cold; slightly soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; both these solvents seem to produce a slight decomposition of the substance when heated with it; very freely soluble in chloroform; freely soluble in benzol or acetone; soluble in ether or glacial acetic acid; slightly soluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol used as described above. Strong sulphuric acid has no action on it in the cold, but when heated with it dissolves some of it with a pale yellow color after it melts; strong hydrochloric acid has no apparent action on it, either hot or cold; strong nitric acid has no action on it in the cold, but dissolves it slightly when hot, and if heated with it for two hours and a half destroys it completely, the only product which we isolated being oxalic acid; on one occasion, however, another product melting near 140° was obtained in small quantity, but we did not feel sufficiently interested in this part of the subject to prepare enough of it to determine whether it was the dinitrite or a tartronic ester. One thing, however, these experiments have established, namely, that the dimalonic-compound is less stable toward nitric acid than the brommalonic-compound, since the latter, after three hours' boiling with the acid, had not gone further than the tartronic ester, while the former usually underwent a total decomposition. On the other hand, the nitrite of the dimalonic-compound is not decomposed by melting, and only slightly by heating with alcohol, and therefore in these two respects is more stable than the nitrite of bromtrinitrophenylmalonic ester.

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[1] This Journal **12**, 20.

The nitrite of trinitrophenylenedimalonic ester shows acid properties. With an aqueous solution of sodic carbonate it gives no action, and very little when alcohol is added, unless in very large quantity, when a yellowish solution is formed; with potassic carbonate in aqueous solution there is no action, but on the addition of alcohol a very strong yellowish brown color; aqueous sodic hydrate gives a reddish solution, on the addition of alcohol an orange flame-colored solution, entirely different in color from that given with the potassic carbonate; ammonic hydrate imparts a strong yellow coloration to the solution, intensified on the addition of alcohol. Upon comparing the acidity of this substance with that of the trinitrophenylenedimalonic ester, it seems as if this latter substance were somewhat more acid than the nitrite, since it gives a slight coloration with aqueous potassic carbonate and seems to act more easily with acid sodic carbonate and alcohol, but the difference between the two in this respect is certainly very slight, which we should not have expected, as it seemed probable that the introduction of the nitrous-acid radicle (ONO) would have increased the ease with which the hydrogen in the other malonic ester radicle was removed.

A solution of the sodium salt of the nitrite of trinitrophenylenedimalonic ester was made by adding one drop of sodic hydrate solution to a large excess of the ester moistened with alcohol, and, after the action had taken place, diluting with much water. The solution thus obtained was of the color of a solution of potassic dichromate, but much less strongly colored than the solutions of the salts of any of the related substances. Its action with the various reagents was tried, and the following characteristic precipitates observed:

With *barium salt*, rather heavy yellow flocks.

With *mercurous* or *lead salts*, heavy yellow flocks.

With *silver* or *copper salts*, yellow flocks.

Salts of *calcium*, *strontium* or *magnesium* gave only faint yellow precipitates, decidedly different from the heavy one produced by baric chloride.

Nitrite of Bromdinitrophenylmalonic Ester,
$C_6H_2Br.(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$.

Although bromdinitrophenylmalonic ester does not change in color when heated with nitric acid, as has been stated more than once in previous papers[1] from this Laboratory, it really is affected in the same way as the corresponding trinitro-compound, being converted into its nitrite, but without the formation of the red secondary product which made the reaction so striking in that case. The substance was prepared as follows: A small quantity of the bromdinitrophenylmalonic ester (melting-point 75°–76°) was heated on the steam-bath with nitric acid of specific gravity 1.38 for five minutes, or longer (as the same compound was obtained if the heating was continued three hours). There was at first no sign of a reaction except a slight evolution of nitrous fumes; but as the heating continued, the undissolved solid melted, forming an oil drop, which after cooling solidified to a mass of crystals, while at the same time the acid liquid deposited crystals looking very much like those of the bromtrinitrophenyltartronic ester. All of these crystals were purified by recrystallisation from boiling alcohol, until they showed the constant melting-point 111°, when they were dried at about 70° and analysed with the following results:

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[1] This Journal **11,** 99; **12,** 8.

I. 0.1973 gram substance gave on combustion 0.2492 gram carbonic dioxide and 0.0510 gram H_2O.

II. 0.2084 gram substance gave 17.4 cc. nitrogen at a temperature of 22° and a pressure of 755.6 mm.

	Calculated for $C_6H_2Br.(NO_2)_2.C.NO_2.(CO_2C_2H_5)_2$.	Found.	
		I.	II.
Carbon	34.66	34.44	...
Hydrogen	2.67	2.87	...
Nitrogen	9.33	...	9.41

The substance therefore is the nitrite of the bromdinitrophenylmalonic ester, and not the corresponding tartronic ester, as we had expected from the long heating used in one of the methods of preparation, and from the fact that no difficulty was encountered in making the combustion of it.

Properties.—The nitrite of bromdinitrophenylmalonic ester crystallises usually in thick rhombic crystals often one millimeter in each direction, which look somewhat like rhombohedra with a sharp acute angle, but are seen to be twins by the lines of twinning and striations; the obtuse angles on these crystals are often truncated. Less commonly with the characteristic forms just described, long flattened prisms occur, which are terminated by a single plane at a sharp acute angle, rarely by two. It is easy to see that the rhombic crystals could be formed by the twinning of these prisms. The crystals are very lustrous, of a white color, with a slight greenish cast, and melt at 111° without decomposition. The substance is essentially insoluble in cold water, very slightly soluble in hot; soluble in cold alcohol, more so, but still far from freely, in hot. It shows no signs of decomposition when boiled with alcohol. It is more soluble in methyl than in ethyl alcohol, cold or hot; very freely soluble in benzol, chloroform or acetone; freely soluble in glacial acetic acid; soluble in ether or carbonic disulphide; nearly, if not quite, insoluble in ligroine.

Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when hot dissolves a little of the substance after it has melted; strong hydrochloric acid has no action, hot or cold; strong nitric acid has no action on it in the cold, but when hot dissolves a little of it, which is deposited on cooling. Neither acid sodic carbonate nor neutral potassic carbonate had any action with it, even in presence of alcohol; sodic hydrate in aqueous solution was without action; if alcohol was added, a portion of the substance dissolved slowly with a yellow color, but most of the white crystals were left unattacked; ammonic hydrate in aqueous solution had no action, with alcohol little or none. The substance behaves, therefore, as we should expect, a salt being formed only by a reagent like sodic hydrate strong enough to remove the nitro group attached to the side-chain.

The nitrite of bromdinitrophenylmalonic ester is much more stable than the corresponding trinitro-compound, since it is not decomposed by boiling with alcohol, or at its melting-point or by boiling with nitric acid; for, as has been already stated, it could be made by boiling for three hours with nitric acid, whereas under these conditions the trinitro-compound was converted into the tartronic ester. Nor did longer boiling of the dinitro-compound with nitric acid produce the tartronic ester, as even after seven hours it showed the melting-point of the unaltered substance 111°. As the trinitrotartronic ester had been obtained also by heating the corresponding nitrite, we tried the same experiment with the dinitronitrite, and found that, when heated a few degrees above its melting-point, it turned rather dark-colored and gave off bubbles of gas, in which bromine was recognised by the smell. The residue was oily, but after solution in alcohol crystals were obtained which showed the characteristic rhombic form of the nitrite of bromdinitrophenylmalonic ester. This experiment therefore seemed to show that the action of heat consisted only in the complete decomposition of a portion of the nitrite of bromdinitrophenylmalonic ester, and, as it did not promise to give the desired tartronic ester, further work in this direction was abandoned.

Reduction of the Nitrite of Bromdinitrophenylmalonic Ester.

The conversion of the nitrite of bromtrinitrophenylmalonic ester into the corresponding tartronic ester by nitric acid, or by the action of heat, indicates that the group NO_2 in the side-chain is attached to the molecule by oxygen instead of nitrogen, or, in other words, that the substance is a nitrite, and not a nitro-compound; but, as we could not consider this a conclusive proof of the oxygen attachment, we have studied the reduction of a body of this class, selecting for this purpose the dinitro-compound, because it is more easily prepared than the corresponding substance containing three nitro groups, and also because the product obtained from it by reduction would probably be more stable than one containing one more amido group.

Six grams of the nitrite of bromdinitrophenylmalonic ester, divided into three lots of two grams each, were mixed with granulated tin, strong hydrochloric acid, and a few drops of alcohol, and after adding a piece of platinum to accelerate the reaction, were allowed to stand on a steam radiator (50°–70°) until all the organic matter had dissolved, and no further action was observed, which happened usually in about an hour and a half. If quantities larger than two grams were used a very dark colored solution was obtained. The solution poured off from the excess of tin was freed from stannous and stannic chlorides by means of sulphuretted hydrogen, when a residue was obtained by evaporation of the filtrate, which gave off ammonia gas when treated with an alkaline hydrate, and formed a precipitate of ammonic chlorplatinate with chlorplatinic acid; it evidently, therefore, contained ammonic chloride in addition to the chloride of the organic base. The washings of the sulphide of tin, which were worked up separately from the filtrate, on the other hand, yielded crystals which showed only a very slight amount of ammonic chloride by the same tests, and accordingly these crystals were dried at 100°, and analysed with the following results;

I. 0.1980 gram substance gave 25.25 cc. nitrogen at a temperature of 23° and a pressure of 764.8 mm.

II. 0.1954 gram substance gave by the method of Carius 0.1480 gram Ag Cl.

	Calculated for $C_6H_3.NH_3Cl(CH.OH.CO.NH)$.	Found.	
		I.	II.
Nitrogen	13.96	14.47	...
Chlorine	17.70	...	18.73

These results are not all that we could wish; but although they show the presence of the small amount of ammonic chloride, which we had detected by the qualitative tests, they leave no doubt in regard to the composition of the organic substance, and therefore we have not thought it worth while to spend the great amount of time which would have been necessary to prepare a sample entirely free from ammonic chloride; especially as these analyses prove that the group NO_2 is attached to the side-chain by oxygen, since we obtained, by the reduction of the nitrite of bromdinitrophenylmalonic ester, ammonic chloride and the chloride of amidoxyoxindol instead of the chloride of diamidoxindol, which would have been formed if the group NO_2 had been attached to the molecule by the nitrogen.

Properties of the Chloride of the Amidoxyoxindol, $C_6H_3.NH_3Cl.(CH.OH.CO.NH)$.

This substance was obtained crystallised in rather large plates, usually in forms like a closed fan terminated by an obtuse angle, and set in rows one over the other with the obtuse angles parallel, or arranged in branching arborescent forms like coral; sometimes in thicker sharp prisms. It had a dark yellow color, as we observed it; was soluble in cold water, more so in hot; slightly soluble in cold or hot alcohol, and insoluble, or nearly so, in most of the other solvents. The strong acids gave no striking reactions with it, except strong nitric acid, which turned it orange-red; but this seemed to be due to some nitrous acid in the nitric, as on the addition of sodic nitrite the color was much intensified. Sodic hydrate added to the aqueous solution gave a few brown flocks, evidently from decomposition of a part of the base; ammonic hydrate gave a tolerably heavy, flocculent precipitate, at first whitish, but turning brown on exposure to the air, but it showed no signs of crystallisation, and with the small amount of substance at our disposal we have been unable to obtain the free base in any definite form. The chloride mixed with alcohol and some strong hydrochloric acid imparted after some time a dark red color to a piece of pine wood.

Attempt to make Dinitrophenylenedimalonic Ester.

The results just described having shown that the behavior of bromdinitrophenylmalonic ester toward nitric acid was not so different from that of the trinitro-compound as we had at first supposed, it became of interest to determine whether other apparent differences between these two bodies were no better marked, and accordingly we tried to make the dinitrophenylenedimalonic ester by the method which had given good results with the trinitro-compound as follows: 3 grams of bromdinitrophenylmalonic ester were dissolved in ether, and, after the addition of 1.5 grams of malonic ester previously treated with 0.15 gram of sodium in a large quantity of alcohol, the mixture was boiled under a return-condenser for three hours; at the end of this time the solution had turned deep red, and a little solid had separated. The product was treated with water and dilute sulphuric acid, the ether separated, and the aqueous liquid tested for sodic bromide, which it was found to contain in small quantity, but the crystals deposited by the ether melted after one crystallisation at 75°–76°, the melting-point of bromdinitrophenylmalonic ester. We infer from this experiment, therefore, that, although a little dinitrophenylenedimalonic ester may have been formed, its quantity was exceedingly small, and that the reaction, if it goes on at all, certainly takes place with much more difficulty in the case of the dinitro- than in that of the trinitro-compound.

LXXIV.—NOTE ON TRIBROMMONONITROBENZOL.

By C. Loring Jackson and W. B. Bentley.

The results of experiments on the behavior of tribromtrinitrobenzol and tribromdinitrobenzol with various reagents have been described in a number of papers from this Laboratory. For the sake of completeness, we felt it necessary to include the tribrommononitrobenzol in our investigation, and were the more inclined to do this as we hoped that it might throw some light on the replacement of bromine by hydrogen, so often observed in our work with the trinitro- and dinitro-compounds. This hope has not, however, been fulfilled, as no such replacement of bromine by hydrogen was observed, and the tribrommononitrobenzol has proved to be so inert with various reagents that it deserves only the short investigation the results of which are given in this paper.

The tribrommononitrobenzol used in this work was prepared by boiling symmetrical tribrombenzol (melting-point 119°) for fifteen minutes with a nitric acid made by adding to fuming nitric acid (specific gravity 1.51) one-quarter of its volume of common strong nitric acid (specific gravity 1.38). The greater part of the tribrommononitrobenzol separated as the mixture cooled, and the rest was obtained by the addition of water to the acid mother-liquor. This process gave better results than when acetic acid was used to dilute the fuming nitric acid according to the method given by V. von Richter.[1]

Action of Tribrommononitrobenzol with Sodic Ethylate.

The tribrommononitrobenzol melting at 125° was acted on by hot sodic ethylate, giving a substance which we found it convenient to prepare as follows: 5 grams of tribrommononitrobenzol dissolved in benzol were mixed with an alcoholic solution of the sodic ethylate from 1 gram of sodium, heated on the water-bath just below boiling for some time, and then allowed to stand at a temperature a little above the ordinary for several hours. The red solution thus obtained was filtered from a precipitate which had formed (this gave a test for bromide with argentic nitrate), diluted with water, and acidified with dilute sulphuric acid, after which the benzol was separated from the aqueous liquid: this was extracted with ether, and the combined extracts from the organic solvents purified by crystallisation from alcohol until the constant melting-point 91° was reached. Sometimes a black tarry product was obtained from the reaction, instead of the white crystals formed if the process had gone well. This tarry mass was worked up most conveniently by distillation with steam, followed by crystallisation of the steam distillate from alcohol. The pure substance was dried at about 70°, and analysed with the following results:

I. 0.1900 gram substance gave by the method of Carius 0.2181 gram AgBr.

II. 0.3800 gram substance gave 15.9 cc. nitrogen at a temperature of 22° and a pressure of 756.5 mm.

	Calculated for $C_6H_2Br_2.NO_2.OC_2H_5$.	Found. I.	II.
Bromine	49.22	48.85	...
Nitrogen	4.31	...	4.72

The substance is therefore dibromnitrophenetol, and was formed by the replacement of one atom of bromine by the ethoxy radicle.

Properties.—The dibromnitrophenetol crystallises in bundles of prisms, which are usually somewhat flattened and terminated by a basal plane, also occasionally showing with this two other planes at an obtuse angle to each other. It is white, but turns brown on exposure to the air; melting-point 91°; essentially insoluble in cold water, perhaps very slightly soluble in hot; alcohol dissolves it sparingly when cold, freely when hot; more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform, acetone, or carbonic disulphide; freely soluble in ether; slightly soluble in cold glacial acetic acid, soluble in hot; very slightly soluble in ligroine. The best solvent for it is hot alcohol. It distils with steam. Strong sulphuric acid has no action in the cold, but when hot gradually forms a black solution; cold nitric acid has no action on it, but when hot dissolves it, depositing crystals on cooling, which seem by their melting-point to be the unaltered substance; strong hydrochloric acid seems to have no action, whether hot or cold; sodic hydrate seems not to act upon it.

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[1] Ber. d. chem. Ges. 8, 1426.

Action of other Reagents on Tribrommononitrobenzol.

Sodic methylate behaved in much the same way as the sodic ethylate, except that it was necessary in this case to heat for a longer time, and even after this a certain amount of tribrommononitrobenzol was apt to be left unaltered. The product after crystallisation from alcohol showed the constant melting-point 104°, but its analyses gave percentages of bromine differing from those corresponding to dibromnitroanisol by about 1 per cent. The cause of this is probably the same as that of the similar want of agreement between the calculated and observed percentages in the case of the bromdinitroresorcin dimethylether;[1] but we have not thought the substance of sufficient importance to try to obtain better analytical results, which, to judge by our work on the bromdinitroresorcin dimethylether, would be a matter of great difficulty.

From these experiments it appears that the tribrommononitrobenzol acts with sodic alcoholates less easily than the tribromdinitrobenzol, which is attacked by them in the cold, forming the ethers of bromdinitroresorcin, whereas it is necessary to heat the mononitro-compound to bring about any action. When the tribromdinitrobenzol is heated with an alcoholate, the third atom of bromine is replaced by hydrogen and an ether of the dinitroresorcin is formed, but we found no trace of any action of this sort with the mononitro compound. It is to be noted, too, that only one atom of bromine is removed from the mononitro-, but two from the dinitro-compound.

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[1] This Journal **13**, 175.

The inertness of tribrommononitrobenzol as compared with the corresponding dinitro-compound is made even more evident by the study of the action of aniline upon it. This substance converts tribromdinitrobenzol into trianilidodinitrobenzol, when heated with it for a short time, whereas the corresponding trinitro-compound is formed in the cold; from the mononitro-substance we were unable to obtain any anilido-compound, even after heating for some time to the boiling-point of aniline; a little aniline bromide was formed, it is true, but almost all of the tribrommononitrobenzol was recovered unaltered, as recognised by its melting-point and very characteristic crystalline form.

No better result was obtained with sodium malonic ester, which acts on the dinitro- and trinitro-compounds in the cold, but even after boiling for some time with the tribrommononitrobenzol yielded only a very small quantity of sodic bromide, while almost all of the tribrommononitrobenzol was recovered unaltered.

Contribution from the Laboratory of General Chemistry, University of Michigan.

ON THE SAPONIFICATION OF THE SUBSTITUTED ACETIC ESTERS.

By Paul C. Freer and F. L. Dunlap.

As the study of organic chemistry has progressed, the influence exerted by negative atoms or groups of atoms upon the compounds in which they enter as constituent parts, has frequently been the subject of remark. It is a well-known fact, for instance, that the introduction of acetyl or carbethoxyl in place of hydrogen in acetic ester renders the remaining hydrogen atoms so reactive that they can act as if they belonged to an acid substance, while a substitution of a nitro-group in methane or ethane can cause a similar change to take place in those bodies.

It seems, *a priori*, then, reasonable to assume that organic acids, like acetic acid, will suffer an increase in their avidity by the introduction of chlorine or bromine in place of hydrogen, and furthermore, this avidity should be greater in the monochlor-acid than in the monobrom-acid, for chlorine is more negative in its nature than bromine, as can readily be seen from the relative stability of the hydrogen compounds of the two halogens, and the same relationship should exist between the dichlor- and dibrom- and the trichlor- and tribrom-acids. That this is the case is shown by the work of Ostwald,[1] who has proved the avidity of the three chlorine substituted acetic acids, as measured by their electric conductivity, to be as follows:

Acetic acid, $K = 0.00189$
Monochlor-acetic acid, $K = 0.155$
Dichlor-acetic acid, $K = 5.17$
Trichlor-acetic acid, $K = 121.$

From these investigations another fact becomes apparent, namely, that the introduction of the first chlorine atom exerts a greater influence than that of the second, while the further substitution of remaining hydrogen atom does not influence the avidity in nearly the same degree as the respective replacement of hydrogen by the other two; for the influence of each successive chlorine atom, beginning with acetic acid, is in the ratio of 86 : 33 : 24. Ostwald further found the constant for monobrom-acetic acid to be 0.138, a number somewhat less than that found with monochlor-acetic acid.

It occurred to us that a similar relationship as was observed by Ostwald in the avidity of the acids in question would be found in their rapidity of saponification; the ethyl ester of the acid displaying the highest constant as determined by Ostwald, should also be most readily saponified, while a successive diminution of this rate should be observed accompanying the elimination of each chlorine atom and its replacement by hydrogen. Some work on the velocity of saponification has been done by Ostwald,[2] who studied the hydrolysis of methyl acetate in presence of various free acids, finding the amount of change in the unit of time much increased by the acid addition. Ostwald studied incomplete reactions, determining the amount of free acid formed from time to time by titration with a standard baryta solution. R. B. Warder[3] also devoted some time to the study of the speed of saponification, using ethyl acetate and sodium hydroxide in dilute aqueous solution. The latter investigator endeavored to discover the relationship between the temperature of a reaction and the velocity thereof, and came to the conclusion that the increase in the speed is approximately as the second power of the temperature, a relationship which agrees with that suspected by Hood[1] from a study of the action of potassium chlorate on ferrous sulphate. Reicher[2] has also undertaken a similar investigation, studying the influence of temperature on the velocity of saponification of acetic ester by means of a solution of sodium hydroxide. He, like Warder, does not complete the reaction, but titrates from time to time, in order to determine the amount of free alkali present.

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[1] Ztschr. phys. Chem. **3**, 176.

[2] J. prakt. Chem. [2] **28**, 449.

[3] This Journal **3**, 340; Ber. d. chem. Ges. **14**, 1361.

Remsen and Hillyer[3] at a later date worked out a method for determining the relative stability of the alkyl bromides, and this was subsequently more fully carried out by Lengfeld.[4] The alkyl bromides, as well as the reagents used, were in alcoholic solution, and the decompositions were studied under the influence of sodium and potassium hydroxides, ammonia, silver nitrate, nitric acid, sulphuric acid and a mixture of silver nitrate and nitric acid. The substances to be decomposed were weighed in small bulbs and sealed. These were then placed in flask, the solution of the reagent added, the flask well stoppered and the bulbs broken. The amount of change was noted by opening sets of the bottles at stated intervals of time and titrating the amount of sodium bromide formed, and the work was carried out at different temperatures, the result showing that the influence of temperature varied with the reaction under consideration. We also arrived at this conclusion after having carried out the series of experiments with the substituted acetic esters, for, as a glance at the appended table will show, this influence is much more apparent in the case of the mono-substituted esters than it is with the di- and tri-substituted ones, and, despite the limited number of results which we are at this time able to present, it seems scarcely possible that the speed of the reactions is approximately as the second power of the temperatures.

The work on the saponification of the substituted esters has, up to the present, only been extended so as to include monochlor-, dichlor- and trichlor-, and monobrom-, dibrom- and tribrom-acetic acids, and has, so far as the relative influence of the halogen atoms upon the speed of the saponification is concerned, fully answered our expectations, for, as will be seen from the plotted curves, the tri-substituted acids are more rapidly saponified than di-substituted ones, and the latter more rapidly than the mono-substituted, and furthermore it becomes apparent that bromine does not exert quite as marked an influence as chlorine. Our work differs from that which has previously been done in two particulars: we used molecular quantities of base and acid, and allowed complete saponification to take place. The results of this research agree with a statement made by Conrad and Brückner[1] that the rapidity of saponification of the esters of the acids of the fatty series increases with the strength of the acid.

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[1] Phil. Mag. [5] **6**, 383.

[2] Ann. Chem. (Liebig) **228**, 257; **232**, 103; **238**, 276.

[3] This Journal **8**, 151.

[4] Ibid. **11**, 40.

Experimental Part.

In the course of this research we studied the saponification of monochlor-, dichlor- and trichlor-acetic esters, and of the corresponding bromine compounds. We endeavored to extend the investigation so as to include the iodo- and nitro-esters, but were compelled to abandon this purpose on account of the instability of the substances in question.

The apparatus used was a modification of that recommended by Beckmann[2] for the determination of molecular weights by the lowering of the freezing-point of solutions, the outer jar being filled with water, which, during any given saponification, was kept at a constant temperature.

The quantity of ester to be saponified was in each case so selected as to be exactly hydrolysed by 5 cc. of a solution of barium hydroxide saturated at 15° C.; 5 cc. of this solution were found to contain 0.22355 gram of barium. The calculated quantities of the various esters which were used in each operation are given below:

For	ethyl monochlor-acetate,	0.2350	gram.
"	ethyl dichlor-acetate,	0.3011	"
"	ethyl trichlor-acetate,	0.3672	"
"	ethyl monobrom-acetate,	0.3203	"
"	ethyl dibrom-acetate,	0.4718	"
"	ethyl tribrom-acetate,	0.6232	"

The amounts of the pure esters necessary for each saponification were respectively weighed into small glass bulbs and sealed for future use.

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[1] Ztschr. phys. Chem. 7, 290.

[2] Ibid. 2, 638.

All of the barium hydroxide solution used in the research was prepared at the same time and was placed in a large bottle fitted with a double-bored stopper and two bent glass tubes, one reaching to the bottom of the flask, the other to the bottom of the stopper. The glass tube which extended into the solution was attached to one of the vents of a double-stopcock burette, while the one terminating at the bottom of the stopper was connected with a wash-bottle containing caustic potash solution; the entrance of carbon dioxide to the top of the burette was prevented by connecting with a tower filled with soda-lime. The bottle containing the baryta solution was placed upon a rack several feet above the level of the table upon which the operations were to be conducted, so that by this means the burette could be emptied and filled at pleasure without allowing any acids which might be present in the atmosphere to come in contact with the standard solution, the value of which was unaltered during the entire research. The apparatus just described is a modification of that devised by Knöfler.

The method for conducting any given saponification was as follows:

Into a large glass test-tube, which extended down into the outer jar of the Beckmann apparatus which was filled with water, one of the small glass bulbs containing a weighed amount of ester was dropped, and 75 cc. of a diluent composed of equal parts of water and alcohol were then added, care being taken to have the diluent exactly at the temperature of the bath. After adding a few drops of phenol phthalein to the contents of the test-tube, the bulb was broken by a glass rod and the mixture agitated until homogeneous; 5 cc. of baryta were then run in, and the interval of time necessary for the disappearance of the color of the indicator noted; the solution in the meanwhile being constantly agitated by means of the glass rod, while the temperature of the bath, which during any saponification was kept constant, was noted. This process was repeated at temperatures ranging from 0° to 60°, the experiments not being carried beyond the latter point, for at about 60° the alcohol begins to be volatilised in such quantities as to affect the volume of diluent. The alcohol used in this work was absolutely free from acid. In the experiments conducted at 0° we, of course, experienced no difficulty in maintaining a constant temperature by means of melting ice, and the bath was brought to the other points by mixing together waters of differing temperatures until the desired one was obtained, and afterward but little trouble was experienced in preventing a variation.

Saponification of Ethyl Monochlor-acetate.

Monochlor-acetic ester was prepared by means of alcohol and dry hydrochloric acid. The substance used had a constant boiling-point from 141° to 142°, and upon analysis gave the following figures:

0.2358 gram ester gave 0.2752 gram AgCl.

	Calculated.	Found.
Cl	28.95	28.86

The results of the saponification were as follows:

Amount of ester, 0.2350 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	84	0°
2	55	8
3	39	14.5
4	27	23
5	17.5	32
6	11	41
7	9	47
8	6	60

Ethyl Dichlor-acetate.

This was prepared in a manner similar to that used for the ethyl monochlor-acetate. The ester has a boiling-point of 156°–157°. An analysis resulted as follows:

0.4011 gram of the ester gave 0.7311 AgCl.

	Calculated.	Found.
Cl	45.19	45.18

Upon saponification, the ester gave the following figures:

Amount of ester, 0.3011 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	9.5	0°
2	8.5	8
3	7.5	15
4	5.75	27
5	3.5	37
6	2.5	46.5
7	1.25	56

Ethyl Trichlor-acetate.

This substance was prepared in the same way as the ethyl monochlor- and dichlor-acetates; it is a colorless liquid with an odor resembling that of oil of wintergreen; its vapors but slightly attack the eyes; its boiling-point is 164°.

0.2173 gram of the ester gave 0.4874 AgCl.

	Calculated.	Found.
Cl	55.58	55.49

The saponification gave the following figures:

Amount of ester, 0.3672 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	7.5	0°
2	5.25	12
3	4.75	15
4	3.25	26
5	1.25	39
6	.5	49
7	.25	55

Ethyl Monobrom-acetate.

The same method was used here as was used in the formation of the preceding esters; however, the addition of hydrochloric acid gas to the alcoholic solution of monobrom-acetic acid causes a slight separation of bromine. For purification, the ester was distilled under diminished pressure, boiling at 73°–75° (40 mm.).

0.1937 gram ester gave 0.2178 AgBr.

	Calculated.	Found.
Br	47.87	47.84

The following results were obtained upon saponification:

Amount of ester, 0.3203 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	90	0°
2	67	8
3	50	15
4	36	24
5	22	36
6	15	43
7	10	52
8	7	60

Ethyl Dibrom-acetate.

This ester was prepared according to the method of Remi[1] by heating bromal with potassium cyanide and alcohol.

Some difficulty was experienced in obtaining a sufficient yield of bromal by following Löwig's method,[2] so that we finally decided upon the following modification, which has shown itself to be entirely satisfactory:

To 150 cc. absolute alcohol, in a flask fitted with an inverted condenser, 135 cc. anhydrous bromine are slowly added by means of a dropping-funnel. After the addition of the bromine, the liquid is boiled upon a water-bath until hydrobromic acid ceases to pass off, when, upon cooling, the liquid separates into two layers. The whole is then placed in a large flask and treated with concentrated sulphuric acid until the violent action accompanied by an evolution of hydrobromic acid has ceased, when a layer of dark-red liquid forms at the bottom of the flask. This portion is separated from the one above and fractioned, the fraction between 165°–180° containing the bromal; and from this, bromal hydrate will separate upon the addition of a small quantity of water and cooling. The hydrate must be kept in the dark in a closed bottle, otherwise slight decomposition sets in.

In order to prepare ethyl dibrom-acetate, the bromal hydrate was treated according to Remi's method,[3] with the difference that after allowing the mixture of bromal hydrate and a saturated alcoholic solution of potassium cyanide to stand for about twenty-four hours, we then finally boiled for some time in a flask fitted with an inverted condenser. Upon fractioning the decanted liquid, the portion boiling between 185°–193° contains the desired ester. To purify this, it was fractioned under diminished pressure, boiling between 101°–102°, 6 mm.

0.2301 gram of the ester gave 0.3513 AgBr.

	Calculated.	Found.
Br	65.01	64.96

The saponification of this ester gave the following figures:

Amount of ester, 0.4718 gram; amount of $Ba(OH)_2$ solution, 5 cc.

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[1] Ber. d. chem. Ges. 8, 695.

[2] Ann. Chem. (Liebig) 3, 288.

[3] Ber. d. chem. Ges. 8, 695.

Experiment.	Time (Minutes).	Temperature.
1	19.5	0°
2	14.0	9
3	10	17
4	7	29
5	5	38
6	3	48
7	2	60

Ethyl Tribrom-acetate.

To the chemically pure tribrom-acetic acid an excess of absolute alcohol was added, and this solution was then saturated with pure, dry hydrochloric acid gas. This whole was then shaken out with water and the precipitated ester separated as nearly as possible from the supernatant liquid and first dried over calcium chloride, and then, after filtering, was finally allowed to stand for several days in a sulphuric-acid desiccator. The ester thus prepared is always slightly colored by bromine; the latter was removed by means of molecular silver. It was found impossible to fraction this ester even *in vacuo*, as considerable decomposition always takes place,—a portion distilling at 139° (38 mm.) upon analysis gave only 80 per cent. of the calculated bromine,—so that we were compelled to use the undistilled product in our work.

The following analysis shows, however, that this was nearly pure:

0.2211 gram of the ester gave 0.3828 AgBr.

	Calculated.	Found.
Br	73.82	73.67

The saponification gave the following results:

Amount of substance, 0.6232 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	17	0°
2	12	10
3	8.5	17
4	6.5	26
5	3.5	38
6	2.0	47
7	1.5	53
8	1.0	60

Finally, ethyl monochlor-acetate was also saponified with 25 cc. diluent to see what influence, if any, the quantity of the latter might have on the reaction.

The results of this saponification, which are given in the following table, show that the figures differ but little from those obtained with a 75-cc. solution.

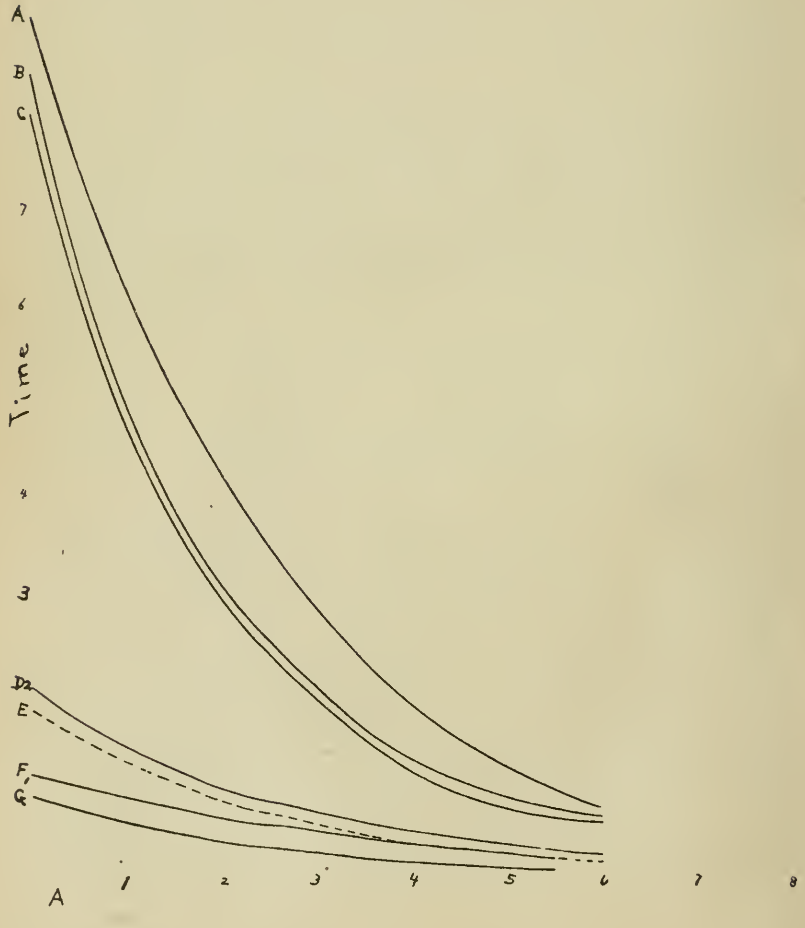
Experiment.	Time (Minutes).	Temperature.
1	80	0°
2	53	8
3	36	15.5
4	24	24.5
5	16	33
6	10	41
7	7.5	52.5
8	5.5	59

A glance at the above results will show that, although the relationship between the times of saponification at any given temperature are not similar to that obtaining between the avidities as developed by Ostwald, yet the acids maintain the same relative positions, namely, those with the greatest avidities are most readily saponified. This can be readily seen by a comparison of the results at 0°:

Monochlor-acetic ester, time,	84	minutes,
Dichlor-acetic ester, time,	9.5	minutes,
Trichlor-acetic ester, time,	7.5	minutes,
Monobrom-acetic ester, time,	90	minutes,
Dibrom-acetic ester, time,	19.5	minutes,
Tribrom-acetic ester, time,	17	minutes.

Another result also becomes apparent, namely, that the introduction of the second chlorine or bromine atom exerts a much greater influence than that of the third. Whether the exact influence exerted by a substituting halogen atom in any compound of the fatty series can, in the future, be calculated by a mathematical formula will only become apparent after an extended investigation of these compounds, although one result can already be predicted, namely, that the influence of the halogen atoms on the rate of saponification will diminish according to their distance from the carbethoxyl group. The discovery that an increase in temperature has a greater relative effect on the speed of saponification of the mono-substituted acids than it has on the di-substituted ones is not unexpected, when we consider that any such acceleration is due to an increase in the molecular motion, and hence to an increasing number of impacts between the base and ether in the unit of time; as a consequence, those molecules with the smallest mass will have their velocity of motion advanced in a greater degree for an equal change in temperature than will those with the larger.

The results of these determinations have been plotted as curves upon the following table, the time of reaction being taken as ordinates and the temperatures as abscissæ:



Contribution from the Chemical Laboratory of the University of Illinois.

I.—A NOTE UPON THE REDUCTION OF SYMMETRICAL TRIAMIDO-TRINITRO-BENZENE.

By Arthur W. Palmer.

In a paper by C. L. Jackson and J. F. Wing upon tribrom-trinitro-benzene published nearly five years ago,[1] the authors record the results of a preliminary attempt to obtain hexamido-benzene, $C_6(NH_2)_6$, by reduction of the symmetrical triamido-trinitro-benzene, $C_6(NH_2)_3(NO_2)_3$, and express the intention of continuing the work, a promise referred to later in a paper upon pentamido-benzene by Jackson and Palmer.[2] At the invitation of Professor Jackson I undertook the study of the reaction, and, although the desired end has not been attained, yet the results seem to be of sufficient interest to warrant a publication of them. The symmetrical triamido-trinitro-benzene used was prepared by the method described by Jackson and Wing,[3] from tribrom-trinitro-benzene prepared according to the directions given in the same article. The tribrom-trinitro-benzene so obtained melted sharply at 285° (uncorrected). By treatment in the cold with alcoholic ammonia for twenty-four hours, then boiling with reverse-cooler for a half-hour, more alcoholic ammonia being added from time to time, the conversion into triamido-trinitro-benzene was completed.

The product, filtered off, was washed with alcohol, then with water and, finally, boiled out several times with chloroform. This product was not analysed, as it in every way corresponded with the product obtained in this same way by Jackson and Wing and analysed by them. The first attempts at reduction were carried out by use of tin and hydrochloric acid, but, as had before been found by Jackson and Wing, the results were unsatisfactory, and it was thought best to try zinc dust and glacial acetic acid, because it was hoped that an acetyl compound would be formed which might be expected to be more stable than the chloride or other salt and consequently more easily handled. It was found, however, that no such acetyl compound was obtained, the product consisting mostly of ammonium chloride (in one case with an unmanageable black tar which may have proceeded from the decomposition of the hexamido-benzene), and this was the result although the mixture was kept cool during the reduction, protected from air, and evaporated, after removal of the zinc, at a pressure of 5 to 7 mm. As these results were so unpromising, the method by treatment with tin and hydrochloric acid was again resorted to. At first an attempt was made to purify the product of the reduction by the method of Nietzki with sulphuric acid and alcohol, but with no favorable result. I accordingly proceeded as follows:

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[1] Proc. Am. Acad. **23**, 142; This Journal **10**, 283.

[2] Proc. Am. Acad. **24**, 105; This Journal **11**, 448.

[3] Loc. cit.

2.06 grams symmetrical triamido-trinitro-benzene, $C_6(NH_2)_3(NO_2)_3$, 15 cc. of alcohol, 25 cc. of hydrochloric acid and the quantity of tin required by theory (8.48 grams) were placed in a flask together. The reaction proceeded slowly, but all of the tin disappeared before the reduction was complete, so 2 grams more tin were added, and after a few days the solution became colorless, and a considerable quantity of white crystalline substance remained in place of the original dark-orange substance. The crystalline substance was filtered off, washed with alcohol, in which it is slightly soluble, then several times with ether, and dried. As it was found to contain tin, it was dissolved in water, the tin removed by sulphureted hydrogen and the filtrate saturated with hydrochloric acid gas. The crystals formed in this way were filtered off and dried. The substance crystallised in long, colorless, acicular prisms which darken gradually when exposed to the air. The aqueous solution quickly turns blue, then, after some time, black, and a black amorphous precipitate separates. An analysis of the crystals led to the identification of the substance as the hydrochloride of pentamido-benzene.

I. 0.1779 gram substance, slightly, but only superficially darkened, gave 0.1859 gram CO_2 and 0.0895 gram H_2O.

II. 0.1453 gram substance gave 33.8 cc. of moist nitrogen gas at 11.8° C. and 745 mm. pressure.

III. 0.1474 gram substance, treated by Carius' method, gave 0.2377 gram AgCl.

	Calculated for $C_6H(NH_2)_5(HCl)_3$.	Found.		
		I.	II.	III.
Carbon	27.43	28.49	...	...
Hydrogen	5.33	5.59	...	...
Nitrogen	26.67	...	27.08	...
Chlorine	40.58	...	...	39.78

As it now seemed that the difficulties met with had been the result of over-reduction, new attempts were made, the only modification of the method being the use of less than the theoretically required quantity of tin. 3.5 grams of pure triamido-trinitro-benzene were mixed with 30 cc. of alcohol and 40 cc. of fuming hydrochloric acid, and 5 grams of tin added: the reaction started at once, and five days later 5 grams more tin were added and the mixture saturated with hydrochloric acid gas.

$$C_6(NH_2)_3(NO_2)_3 + 9Sn + 18HCl = C_6(NH_2)_6 + 6H_2O + 9SnCl_2.$$

By a study of the course of the reaction it was found from direct tests that the chief product of the reaction is $SnCl_2$ and that only very small quantities of $SnCl_4$ are at any time formed:

$$2C_6(NH_2)_3(NO_2)_3 + 9Sn + 36HCl = 2C_6(NH_2)_6 + 12H_2O + 9SnCl_4.$$

According to the equation, the quantity of tin required by theory for reduction of 3.5 grams of triamido-trinitro-benzene is 14.38 grams. When the tin had entirely disappeared, the liquid, although deeply colored and containing much of the triamido-trinitro-benzene still unchanged, was saturated with hydrochloric acid gas and the precipitate filtered off and washed with fuming hydrochloric acid and then with alcohol. The residue, on a Gooch filter, was extracted with water, which left the triamido-trinitro-benzene undissolved—the filtered solution treated with sulphureted hydrogen until all the tin was precipitated, and the solution, now free of tin, saturated with hydrochloric acid gas. The crystals which separated gave all of the reactions of pentamido-benzene hydrochloride, and some of the product was analysed with the following results:

I. 0.2016 gram substance yielded 0.2032 gram CO_2 and 0.1044 gram H_2O.

II. 0.1350 gram substance gave 34.4 cc. of moist nitrogen gas at 22° C. and 744 mm. pressure.

	Calculated for $C_6H(NH_2)_5(HCl)_3$.	Found.	
		I.	II.
Carbon	27.43	27.49	...
Hydrogen	5.33	5.75	...
Nitrogen	26.67	...	27.51
Chlorine	40.58	...	...

Another reduction, run in the same way, but by use of 15 grams of tin to 5.75 grams of triamido-trinitro-benzene, resulted similarly, but the product was not analysed. Theory requires for 5.75 grams of triamido-trinitro-benzene 23.69 grams of tin.

The results herein noted appear to establish the fact that upon reduction of triamido-trinitro-benzene, $C_6(NH_2)_3(NO_2)_3$, at least one amido group or one nitro group is replaced by hydrogen—a result similar to that already noticed by Nietzki[1] and Hagenbach in their attempt to obtain pentamido-benzene by reduction of their mononitro-derivative of diethenyl-tetramido-benzene.

ON THE FORMATION OF LAYERS IN SOLUTIONS OF SALTS IN MIXTURES OF WATER AND ORGANIC LIQUIDS.

By C. E. Linebarger.

It has been known for a very long time that if potash be added to weak alcohol, two well-defined layers will separate out, the upper one consisting of a little of the salt, dissolved in a mixture of little water and much alcohol, and the lower one of the greater part of the salt dissolved in a mixture of much water and little alcohol. This has been turned to practical account in the concentration of alcohol. Raymond Lully (A. D. 1235) seems to be the first chemist, or rather alchemist, who makes mention of the phenomenon, but it was probably known long before his time, as little originality is to be found in his writings.

We find no record of the phenomenon with other salts than potash, or other liquids than alcohol, up to the year 1830, when Brandes,[2] in the course of an investigation on the hydrates of manganous sulphate, observed that under certain conditions of temperature and concentration in a solution of manganous sulphate in a mixture of alcohol and water, a layer like a heavy oil collects at the bottom of the vessel. Brandes merely makes passing mention of the fact and does not concern himself about its explanation. Some thirty years afterwards Hugo Schiff[3] rediscovered the fact.

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[1] Ber. d. chem. Ges. **20**, 331, 2114.

[2] Ann. der Phys. Pogg. **20**, 586.

[3] Ann. Chem. (Liebig) **118**, 362.

In determining the solubility of certain salts in mixtures of alcohol and water of varying strengths, he found that a 15 to 50 per cent. spirit, when saturated with manganous sulphate, separated into two layers, the lower one containing much salt and little alcohol, the upper one much alcohol and little salt. This separation does not take place at the ordinary temperature, when an alcohol of less than 15 or more than 50 per cent. is taken.

At a higher temperature, however, layers form even with an alcohol of 13 per cent. or one of 60 per cent. and between. Experiments showed that if 100 volumes of solvent be saturated with manganous sulphate, the upper layer occupied:

When 20 per cent. spirits was used, 16 volumes.
“ 30 “ “ “ “ “ 44 “
“ 40 “ “ “ “ “ 66 “

Percentage of alcohol, ...	20	30	40
Percentage weight of salt dissolved, upper layer,	2.2	1.66	1.31
Percentage weight of salt dissolved, lower layer,	47	48	48.6

And the upper layers contain from 50 to 55 per cent. alcohol; the lower, 12 to 14 per cent.

The above is essentially all that Schiff did on the subject, and matters rested so until 1887, when J. Traube and O. Neuberg[1] took up the subject, and found that many other salts had this peculiarity of causing their solution in alcohol and water to separate into layers. They examined more closely the layers formed in a system consisting of ammonium sulphate, alcohol and water, in order to see if the layers were formed in molecular proportions. Although their experimental data are insufficient to permit the drawing of any general conclusions, yet they estabished the following facts, viz., as the temperature increases—

1) in the upper layer, there is a decrease in the amount of salt and water and an increase in the amount of alcohol;

2) in the lower layer, the amount of water increases and the amount of salt and alcohol decreases.

As the change in the composition of the lower layer is, however, so insignificant, even when the temperature changes considerably, they think that the composition of the lower layer may be regarded as approximately constant.

They found further that, as the amount of salt or alcohol increases (even at different temperatures) there is—

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[1] Ztschr. phys. Chem. **1**, 509.

1) in the upper layer a decrease in the amount of water and salt and an increase in the amount of alcohol;

2) in the lower layer, a decrease in the amount of alcohol and an increase in the amount of salt, while the amount of water first increases, then decreases.

The question whether or not the layers have a composition according to molecular proportions could not be answered decisively.

Pharmacists[1] have observed that, in filling certain prescriptions, a separation into layers takes place. For instance, if chloral be added to a solution of potassium bromide in weak spirits, layers separate out. Likewise layers are formed when potassium acetate is added to the fluid extract of buchu. In this connection may be mentioned the observation made by Parmentier[2] that certain complex inorganic acids are soluble in ether only within certain limits, an excess of the solvent causing a separation into layers. I have found also that many organic substances have this property of forming layers. Thus cane-sugar in aqueous solution forms layers with alcohol and with acetone; glycerine in alcoholic solution forms layers if ether and benzene be added; and such instances might be greatly multiplied.

Here, then, is a class of phenomena of solutions of which but relatively little is known. All investigations on the subject have been carried out with but few salts and ethyl alcohol. J. Traube and C. Neuberg having found[3] that methyl alcohol does not, and isoamyl alcohol does bring about the formation of layers in an aqueous solution of ammonium sulphate, say that perhaps similar phenomena might be observed in other organic series. The conditions of layer-formation seem to be two freely miscible liquids and a substance quite soluble in one and insoluble in the other. But one cannot say that any substances that fulfill these conditions will form layers. Heretofore the liquids have been ethyl alcohol and water; the substances, manganous sulphate (Schiff), ammonium sulphate (Traube and Neuberg) and potassium carbonate. I have taken up the subject with the intention of finding out what substances are capable of forming these layers, what the limits of layer-formation are, and what the composition of the layers may be. I have limited myself thus far to four organic liquids—methyl alcohol, ethyl alcohol, propyl alcohol, and acetone—all of which are freely soluble in water, and to about seventy typical salts. I will divide the subject into three parts: 1. The examination of the behavior of the salts towards mixtures of water and the above organic liquids as regards the formation of layers. This part is essentially qualitative. 2. The determination of the limits of the formation of layers under varying conditions of temperature and concentration. 3. The determination of the composition of the two layers together with their specific gravities and surface tensions.

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[1] Private communication by Prof. Miner of Illinois College of Pharmacy.

[2] Compt. rend. **104**, 686.

[3] Ztschr. phys. Chem. **1**, 514.

PART I.

The experiments were carried out as follows: To a saturated solution of a salt contained in a test-tube the organic liquid was added little by little, with vigorous agitation, until either a layer formed or the salt was precipitated. In the cases where no layer formed, the liquid added would sometimes readily mix with the water, forming a quite good solvent for the salt, so that it was necessary to add a relatively large amount to bring about precipitation, and sometimes the first drops added would cause a precipitate to form. It is necessary to work with very concentrated solutions and to add the organic liquid slowly, since some of the salts form layers only within narrow bounds, which cannot be detected except by operating carefully. All the experiments were repeated with a solution of the salt half as concentrated, entirely similar results, with one or two exceptions, being obtained.

The results of the experiments are given in the following table, in which the first column gives the name of the salt and the second its chemical formula.

Table.[1]

Name of Salt.	Formula.	$CH_3.OH$.	$C_2H_5.OH$.	$C_3H_7.OH$.	$(CH_3)_2CO$.
Lithium chloride,	$LiCl$	n	n	n	$y\,!$
Ammonium "	NH_4Cl	n	n	y	$y\,!$
Sodium "	$NaCl$	n	n	$y\,!$	$y\,!$
Potassium "	KCl	n	n	$y\,!$	$y\,!$

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[1] y = forms layers with water and the organic liquid at the head of the column.
n = forms no layers as above given.
$y\,!$ = layers are formed within wide limits.
y_n = layers are formed only within narrow limits.
n_e = forms no layers; salt is quite soluble in a mixture of water and organic liquid.
n_p = forms no layers; salt is quite insoluble in a mixture of water and organic liquid.

Name of Salt.	Formula.	$CH_3.OH$.	$C_2H_5.OH$.	$C_3H_7.OH$.	$(CH_3)_2CO$.
Rubidium chloride,	$RbCl$	n_e	n_e	y !	y !
Calcium “	$CaCl_2$	n_e	n_e	y	y !
Strontium “	$SrCl_2$	n_e	n_e	n_e	y
Barium “	$BaCl_2$	n_e	n_e	n_e	n
Nickel “	$NiCl_2$	n_e	n_e	n_e	n_e
Cobalt “	$CoCl_2$	n_e	n_e	n_e	y_w
Copper “	$CuCl_2$	n_e	n_e	n_e	y_w
Cerium “	$CeCl_4$	n_e	n_e	n_e	n_e
Aluminium “	Al_2Cl_6	n	n	n	n
Ferric “	Fe_2Cl_6	n_e	n_e	n_e	n_e
Manganese “	$MnCl_2$	n_e	n_e	n_e	y !
Cadmium “	$CdCl_2$	n_e	n_e	n_e	n_e
Zinc “	$ZnCl_2$	n_p	n_p	n_p	n_p
Mercuric “	$HgCl_2$	n_e	n_e	n_e	n_e
Magnesium “	$MgCl_2$	n_e	n_e	n_e	n_e
Stannous “	$SnCl_2$	n	n	n	n
Ammonium acetate,	$NH_4(C_2H_3O_2)$	n_e	n_e	n_e	n_e
Sodium “	$NaC_2H_3O_2$	n_e	n_e	n_e	n_e
Potassium “	$KC_2H_3O_2$	n_e	n_e	n_e	y !
Nickel “	$Ni(C_2H_3O_2)_2$	n_e	n_e	n_e	n_e
Manganese “	$Mn(C_2H_3O_2)_2$	n_e	n_e	n_e	y
Magnesium “	$Mg(C_2H_3O_2)_2$	n_e	n_e	n_e	n_e
Lead “	$Pb(C_2H_3O_2)_2$	n_e	n_e	n_e	n_e
Ammonium nitrate,	NH_4NO_3	n_e	n_e	n	n
Sodium “	$NaNO_3$	n_e	n_e	y !	n_e
Potassium “	KNO_3	n_p	n_p	n_p	n_p
Calcium “	$Ca(NO_3)_2$	n_e	n_e	n_e	n_e
Strontium “	$Sr(NO_3)_2$	n_e	n_e	y	n_e
Barium “	$Ba(NO_3)_2$	n_p	n_p	n_p	n_p
Magnesium “	$Mg(NO_3)_2$	n_e	n_e	n_e	n_e
Nickel “	$Ni(NO_3)_2$	n_e	n_e	n_e	n_e
Cobalt “	$Co(NO_3)_2$	n_e	n_e	n_e	n_e
Mercurous “	$Hg(NO_3)$	n_e	n	n_p	n_p
Lead “	$Pb(NO_3)_2$	n_p	n_p	n	n_p
Lithium sulphate,	Li_2SO_4	n_p	n_p	y !	y !
Sodium “	Na_2SO_4	n_p	y	y !	y
Potassium “	K_2SO_4	n	n	n	n
Ammonium “	$(NH_4)_2SO_4$	n	y	y	y

Name of Salt.	Formula.	$CH_3.OH$.	$C_2H_5.OH$.	$C_3H_7.OH$.	$(CH_3)_2CO$.
Nickel sulphate,	$NiSO_4$	n_p	n_p	y	y !
Cobalt “	$CoSO_4$	n_p	n_p	y_w	y
Copper “	$CuSO_4$	n_p	n	y !	n_p
Ferrous “	$FeSO_4$	n	n ?	y !	n_p
Ferric “	$Fe_2(SO_4)_3$	n_e	n_e	y_w	y_w
Cadmium “	$CdSO_4$	n_e	y_w	y	y
Zinc “	$ZnSO_4$	n	y	y	y
Chromium “	$Cr_2(SO_4)_3$	n_e	n_e	n	n
Manganese “	$MnSO_4$	n	y !	y !	y !
Ammonium hydrate,	NH_4OH	n_e	n_e	n_e	n_e
Sodium “	$NaOH$	n	y_w	y !	y !
Potassium “	KOH	n	y_w	y !	y !
Barium “	$Ba(OH)_2$	n	n_p	n_p	n_p
Ammonium carbonate,	$(NH_4)_2CO_3$	n_e	n	n_p	n_p
Sodium “	Na_2CO_3	n	y !	y !	y !
Potassium “	K_2CO_3	y_w	y !	y !	y !
Lithium “	Li_2CO_3	n_p	n_p	n_p	n_p
Sodium bicarbonate,	$NaHCO_3$	n_p	n_p	n_p	n_p
Cadmium iodide,	CdI_2	n_e	n_e	n_e	n_e
Potassium “	KI	n_e	n_e	n_e	n_e
Sodium “	NaI	n_e	n_e	n_e	n_e
Ammonium bromide	NH_4Br	n_e	n_e	n_e	n_e
Sodium “	$NaBr$	n_e	n_e	n_e	n_e
Potassium “	KBr	n_p	n_p	n_p	n_p
Potassium cyanide,	KCN	n_e	n_e	y !	y !
Potassium ferricyanide,	K_3FeCy_6	n_p	n_p	y_w	n_p
Potassium ferrocyanide,	K_4FeCy_6	n_p	n_p	n_p	n_p
Magnesium bromide,	$MgBr_2$	n_e	n_e	n_e	n_e

The table shows certain regularities in regard to the formation of layers. The chlorides generally do not exhibit this phenomenon. The group of the chlorides of the alkaline metals are, however, a notable exception. All of these form layers in a mixture of acetone and water, and, save lithium, in a mixture of propyl alcohol and water. It is seen also that the higher the molecular mass, the wider are the limits of layer-formation; and the table shows that lithium chloride with the smallest molecular mass does not form layers in propyl alcohol, while ammonium chloride possessing the next smallest molecular mass does so within quite narrow limits. It would seem, then, that there is an intimate relation between the molecular masses and the capability of causing a separation into two layers in solutions; in the case of the alkaline chlorides, the smaller the molecular mass, the less pronounced this peculiarity of layer-formation. The chlorides of the alkaline earths, on the other hand, behave in exactly the opposite way. Here the smaller the molecular mass, the more readily does the formation of layers take place. Thus, calcium chloride (molecular mass = 111) forms layers in mixtures both of propyl alcohol and water and of acetone and water; strontium chloride (molecular mass 158.5) only in mixtures of acetone and water, while barium chloride (molecular mass = 208) forms no layers at all. There is, therefore, a regular gradation according to the molecular masses of the chlorides. It is noteworthy that manganese chloride forms well-defined layers with acetone and water.

With but few exceptions, the acetates and nitrates do not cause a separation into layers. It is worth while to note that the salts sodium nitrate and strontium nitrate, that form layers in mixtures of propyl alcohol and water by exception, contain as base those elements which are the second members in the triads: lithium, *sodium*, potassium; calcium, *strontium*, barium.

But the sulphates and carbonates exhibit this peculiarity of layer-formation in the most marked degree. Thus sodium and potassium carbonates form layers within wide limits with ethyl and propyl alcohols and acetone. Potassium carbonate, however, is the only salt forming layers with methyl alcohol, and that, too, within narrow limits.

The alkali sulphates—with the exception of potassium sulphate, which owes its behavior to its slight solubility—form layers in mixtures of propyl alcohol and water and of acetone and water, as well as in mixtures of ethyl alcohol and water. To this last statement lithium sulphate, however, forms an exception. The rest of the sulphates examined all form layers, except chromium sulphate, with propyl alcohol and water, and copper, ferrous and chromium sulphate, with acetone and water. Only with zinc, manganese and cadmium sulphates are layers with ethyl alcohol and water obtained.

Sodium and potassium hydrates form layers in mixtures of the three organic liquids, respectively, with water.

Taking now the organic liquids into consideration, we see that only methyl alcohol forms layers with potassium carbonate. Ethyl alcohol and water together with several salts form layers, while propyl alcohol and water, and acetone and water form layers with a still greater number of salts. It is seen that without exception any salt that forms layers in a mixture of ethyl alcohol and water, does so also in mixtures of propyl alcohol and water, and acetone and water, and the layers are generally formed within wider limits. In the case of the alcohols, then, the greater the molecular mass, the more pronounced the formation of layers. Propyl alcohol and acetone which have almost equal atomic masses do not, however, behave in the same way as regards the formation of layers. Thus in the case of the chlorides and acetates, acetone sometimes causes the formation of layers, where propyl alcohol does not, while in the case of the nitrates just the opposite takes place. The property of forming layers seems to depend upon the nature of the acid part of the salt and not upon its base.

PART II.

The formation of layers in a system consisting of a salt, an organic liquid and water takes place only within certain limits. This second part of the investigation gives these limits for certain salts which possess in a marked degree the peculiarity of forming layers in mixtures of (1) ethyl alcohol and water, (2) propyl alcohol and water, (3) acetone and water.

Determination of the "Upper" Limit of Layer-formation.

By "upper" limit is meant the limit attained when the formation of a layer is rendered impossible by the presence of too much organic liquid. Experimentally it was difficult to determine this limit with any degree of accuracy. As the alcohol or acetone, as the case may be, becomes more concentrated, the salt becomes more insoluble and generally separates out before the limit is reached. Although I tried several salts, it was only with potassium carbonate that I was able to obtain trustworthy data. With the other salts, crystallisation always took place long before the true limit was attained, so that layers and solid salt were present at the same time.

The determinations were carried out as follows: A certain volume of a titrated solution of salt was introduced into a graduated tube such as is used in gas analysis, and small quantities of organic liquid added from time to time. After the addition of each portion of alcohol or acetone, the contents of the tube were vigorously agitated and the tube placed in a vertical position in a place where the temperature varied but little. After a couple of hours the volumes of the layers were read off and alcohol again added. This was continued until no layer remained at the bottom of the tube. As stated above, all the salts with the exception of carbonate of potassium were precipitated before the layer disappeared. In the case of this latter salt, crystals appeared as soon as the layer disappeared.

I give the results of a determination carried out with potassium carbonate, ethyl alcohol and water.

4 cc. of solution were taken containing 0.592 gram K_2CO_3 and 3.8 grams H_2O.

Successive additions of alcohol,	6 cc.	6	4	4	6	8	12	10	5	5	4
Total alcohol added,	6 cc.	12	16	20	26	34	46	56	61	66	70
Volume of upper layer,	8.6 cc.	15.6	18.6	23.	29.8	36.9	49.2	59.7	62.	66.4	70.6
Volume of lower layer,	1.1 cc.	1	0.9	0.8	0.6	0.5	0.	30.2	0.1	0.1	0

As 70 cc. of the alcohol used contain 1.75 grams water and 54.5 grams absolute alcohol, the upper limit is reached in a system consisting of 54.5 grams alcohol, 5.5 grams water, and 0.592 gram potassium carbonate.

Two other determinations, made by adding at once nearly enough alcohol to cause the disappearance of the lower layer, and then approaching by small quantities the requisite amount, gave:

I. 54.1 grams alcohol; 5.5 grams water; 0.592 gram carbonate.
II. 53.8 grams alcohol; 5.3 grams water; 0.592 gram carbonate.

Considering the difficulties of the determinations, the agreement can be regarded as entirely satisfactory.

Determination of the "Lower" Limit of Layer-formation.

By "lower" limit is understood the point where a layer ceases to form, on account of the presence of an excess of water. The determinations of this limit can be made with great accuracy. If water be added slowly to a solution separated into layers, at the point where it is impossible to distinguish them as such the solution turns milky; also when a layer commences to form, this same milkiness is apparent. But a single drop of water is necessary, when the limit is reached, to cause the solution to become perfectly clear. The determinations were accordingly made as follows: Varying quantities of organic liquid and water were added from burettes to a titrated solution of a salt until a drop of water would clear up the milkiness caused by a drop of alcohol. So sharply defined is this point that a single drop of alcohol caused a distinct cloudiness in a clear solution of potassium carbonate just ready to separate into layers.

The details of the operation are the following: A known volume of a titrated salt solution was run into a bottle fitted with a good glass stopper. A little organic liquid was then run in from a burette and enough water added to render the solution clear. The bottle was then placed in a thermostat, and when its contents had acquired the desired temperature, enough of the organic liquid was added to cause a cloudiness to appear. The bottle was then replaced in the thermostat. If its contents again became clear a little more organic liquid was added. This was repeated until a *drop* of water would clear up the milkiness occasioned by a drop or so of alcohol. The burettes were then read off and the process repeated by adding more organic liquid and water. After a little experience the determinations can be made very accurately and quickly.

When comparatively large quantities of organic liquid and water had been added, the point where the solution turned milky was not so easy to discern. But as, before this point was reached, enough determinations could be made to show the behavior of the solution, that circumstance has but little weight.

As temperature had no little influence upon the formation of layers, before giving the results of my determinations I will describe some experiments made with the intention of finding out just what this influence was.

Influence of Temperature upon the Formation of Layers.

In general, it may be stated that the lower the temperature the more water is needed to bring about the disappearance of the layers. A fall of a few degrees of temperature will bring about the characteristic cloudiness in a solution of potassium carbonate in a mixture of alcohol and water just on the point of forming layers, and this cloudiness will disappear on warming to the previous temperature. The experiments were carried out with potassium carbonate, ethyl alcohol and water.

I placed in each of four glass-stoppered bottles 10 cc. of solution containing 1.48 grams K_2CO_3 and 9.5 grams water, and then added (1) to first bottle 20 cc. alcohol (= 15.6 grams C_2H_6O and 0.5 gram H_2O); (2) to second bottle 30 cc. alcohol (= 23.4 grams C_2H_6O and 0.75 gram H_2O); (3) to third bottle 40 cc. alcohol (= 31.2 grams C_2H_6O and 1 gram H_2O); (4) to fourth bottle 50 cc. alcohol (= 39 grams C_2H_6O and 1.25 grams H_2O).

The bottles were heated in a thermostat to 55.5° C. and water added until the cloudiness just disappeared. It was found necessary to add to

	(1)	(2)	(3)	(4)
Water in cc.	6.8	11.3	15.7	18.9

The temperature was then allowed to fall to 19.4° C., when, to cause the ensuing cloudiness to disappear, I had to add to

	(1)	(2)	(3)	(4)
Water in cc.	1	1.4	1.9	3.2

I prepared another similar set of bottles, heated them to 44° C., and added, to just cause turbidity, to

	(1)	(2)	(3)	(4)
Alcohol in cc.	1.1	1.7	2.1	2.5

On raising the temperature to 61.6° it was necessary to add to

	(1)	(2)	(3)	(4)
Alcohol in cc.	0.5	0.7	0.9	1.1

The results of the experiments are regular and entirely concordant among themselves. They show how great is the influence of temperature, and that it is necessary, in order to obtain strictly comparable results, to take it into account. In all the determinations I made the temperature of the solutions was 20° C.

The results of the determinations of the lower limits of the formation of layers are given in the following tables. These need no special explanation, with the exception perhaps of the last two columns. Here "water × const." and "alcohol × const." indicates that the water and alcohol are multiplied by a number which is the reciprocal of the weight of the salt. The quantities of alcohol and water are thus referred to unit weight of salt, which renders all the tables comparable.

The salts used were all by individual tests found to be strictly chemically pure. A concentrated solution was made of each, and the salt therein determined gravimetrically. By taking the specific gravity of the solution, the amount of water present was easily determined. The methyl alcohol was from the establishment of Kahlbaum and labeled "*puriss. acetonfrei.*" Its specific gravity at 18° was 0.7953. The ethyl alcohol was prepared by distilling ordinary spirits over quicklime. Its specific gravity at 15° was 0.8002, and, therefore, contained two per cent. of water by weight; a correction is made for this water in the tables. The propyl alcohol was chemically pure, with a specific gravity of 0.8075 at 15°. The acetone was chemically pure and had a specific gravity of 0.796 at 15°.

I.—*Potassium carbonate; methyl alcohol; water.*

2 cc. of solution containing 1 gram K_2CO_3 and 1.63 grams H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.
I	0.64	2.27	3.2	2.54
II	0.87	2.5	4.1	3.26
III	1.6	3.23	8.5	6.76

II.—*Potassium carbonate; ethyl alcohol; water.*

1 cc. of solution containing 0.148 gram K_2CO_3 and 0.95 gram H_2O.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Absolute Alcohol in grams.	Water ×7.	Alcohol ×7.
I	2.15	0.15	3.25	5.	3.85	22.7	26.9
II	3.72	0.29	4.96	10.1	7.77	34.7	53.3
III	5.1	0.45	6.5	15.5	11.95	45.5	83.6
IV	6.4	0.6	7.95	20.	15.4	55.6	107.8
V	7.6	0.78	9.33	25.	19.22	65.3	134.5
VI	8.7	0.9	10.55	30.	23.1	73.8	161.7

III.—*Potassium carbonate; propyl alcohol; water.*

1 cc. of solution containing 0.148 gram K_2CO_3 and 0.95 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 7.	Alcohol × 7.
I	0.95	1.90	1.6	1.28	13.3	8.9
II	4.1	5.05	7.9	6.34	35.3	44.3
III	5.5	6.45	11.9	9.54	45.1	66.7
IV	5.8	6.75	12.6	10.	47.2	70.
V	9.3	10.25	24.5	19.6	71.7	137.2

IV.—*Potassium carbonate; acetone; water.*

1 cc. of solution containing 0.5 gram K_2CO_3 and 0.88 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 2.	Acetone × 2.
I	3.72	4.60	3.	2.4	9.2	4.8
II	7.2	8.08	7.4	5.92	16.1	11.4
III	10.2	11.08	11.8	9.44	22.1	18.8
IV	14.65	15.53	19.3	15.44	31.1	30.8
V	18.4	19.28	26.9	21.52	38.5	43.

V.—*Potassium carbonate; acetone; water.*

2 cc. of solution containing 0.296 gram K_2CO_3 and 1.9 grams H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 3.4.	Acetone × 3.4.
I	1.12	3.02	2.	1.6	10.2	5.4
II	3.65	5.55	5.3	4.24	18.8	14.4
III	6.55	8.45	10.4	8.32	28.7	28.2
IV	9.5	11.4	18.4	14.72	38.7	50.0
V	12.8	14.7	33.	26.4	49.9	89.7

VI.—*Sodium carbonate; ethyl alcohol; water.*[1]

1 cc. of solution containing 0.293 gram Na_2CO_3 and 0.98 gram H_2O.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Absolute Alcohol in grams.	Water × 3.4.	Alcohol × 3.4.
I	7.7	0.27	8.95	9	6.93	30.4	23.6
II	9.8	0.34	11.12	11.6	8.94	37.8	30.4
III	13.4	0.58	14.96	19	14.62	50.86	49.7
IV	15.2	0.79	16.97	25.5	19.61	57.7	66.7

VII.—*Sodium carbonate; propyl alcohol; water.*

1 cc. of solution containing 0.293 gram Na_2CO_3 and 0.98 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 3.4.	Alcohol × 3.4.
I	3.85	4.84	2.4	1.94	16.4	6.5
II	7.2	8.18	7.3	5.91	27.8	20.0
III	9.	9.98	10.6	8.59	33.9	29.2
IV	13.8	14.78	20.7	16.76	50.2	56.9
V	15.95	16.93	25.8	20.89	57.5	71.0
VI	18.7	19.68	33.	26.73	66.9	90.7

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[1] Near the point of layer-formation, crystals separated out; that is, sodium carbonate is not very soluble in alcohol and water mixed in about the proportions necessary to produce layers. Hence the determinations in the above table are only approximately correct. They were made by adding alcohol rapidly to the solution containing an excess of water, and reading off without waiting long, so as to avoid the error due to the formation of the solid salt.

VIII.—*Sodium carbonate; propyl alcohol; water.*

0.5 cc. of solution containing 0.4165 gram Na_2CO_3 and 0.49 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 6.8.	Alcohol × 6.8.
I	5.	5.49	5.7	4.62	37.4	30.4
II	10.2	10.69	18.5	14.98	72.7	102.
III	12.7	13.19	25.5	20.65	89.7	140.7

IX.—*Sodium carbonate; acetone; water.*

1 cc. of solution containing 0.293 gram Na_2CO_3 and 0.98 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 3.4.	Acetone × 3.4.
I	4.85	5.83	3.4	2.73	19.8	9.2
II	7.5	8.48	6.2	4.96	28.8	16.8
III	10.75	11.73	10.2	8.16	39.8	27.7
IV	13.7	14.68	14.15	11.32	49.9	38.4
V	16.4	17.38	18.9	15.12	59.1	51.3
VI	18.9	19.88	23.2	18.56	67.5	63.1
VII	21.	21.98	27.5	22.00	74.8	74.8

X.—*Sodium carbonate; acetone; water.*

0.5 cc. of solution containing 0.1465 gram Na_2CO_3 and 0.49 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 6.8.	Acetone × 6.8.
I	3.9	4.39	3.1	2.48	28.85	16.8
II	7.9	8.39	8.	6.4	57.55	43.5
III	8.4	8.89	8.6	6.88	60.4	46.9
IV	11.1	11.59	13.	10.4	78.8	70.7
V	15.	15.49	20.7	16.56	105.4	98.

XI.—*Ammonium sulphate; ethyl alcohol; water.*

1 cc. of solution containing 0.4084 gram $(NH_4)_2SO_4$ and 0.8 gram H_2O.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 2.5.	Alcohol × 2.5.
I	0.7	0.02	1.52	0.8	0.62	3.8	1.5
II	1.75	0.07	2.62	2.2	1.7	6.5	4.3
III	2.6	0.1	3.5	3.5	2.7	8.7	6.8
IV	3.95	0.18	4.93	6.25	4.82	12.3	12.1
V	6.56	0.37	7.73	12.8	9.87	19.3	24.7
VI	8.4	0.54	9.74	17.3	13.3	24.3	33.3
VII	15.4	1.22	17.42	40.8	31.42	43.4	78.5

XII.—*Ammonium sulphate; propyl alcohol; water.*

1 cc. of solution containing 0.4084 gram $(NH_4)_2SO_4$ and 0.8 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 2.5.	Alcohol × 2.5.
I	3.3	4.1	1.4	1.12	10.7	2.8
II	6.8	7.6	7.5	6.0	19.0	15.0
III	8.4	9.2	11.	8.8	23.0	22.0
IV	12.1	12.9	20.8	16.64	32.2	41.6
V	15.3	16.1	30.9	24.72	40.2	61.8
VI	16.6	17.4	35.7	28.56	43.5	71.4

XIII.—*Ammonium sulphate; acetone; water.*

1 cc. of solution containing 0.4084 gram $(NH_4)_2SO_4$ and 0.8 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 2.5.	Alcohol ×2.5.
I	1.75	2.5	1.2	.96	6.4	2.4
II	5.	5.8	5.	4.	14.5	10.0
III	8.9	9.7	10.6	8.48	24.2	21.2
IV	13.2	14.	19.5	15.6	35.0	39.0
V	17.4	18.2	29.	23.2	45.5	58.0

XIV.—*Sodium sulphate; propyl alcohol; water.*

1 cc. of solution containing 0.1622 gram Na_2SO_4 and 0.98 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol. in grams	Water × 6.2.	Alcohol × 6.2.
I	3.65	4.63	4.2	3.36	28.5	20.8
II	6.2	7.18	9.1	7.28	44.5	44.1
III	8.9	9.88	15.5	12.4	61.2	76.8
IV	11.7	12.68	20.65	16.52	78.6	102.4
V	13.3	14.28	27.3	22.04	88.5	136.6
VI	16.45	17.43	36.8	29.44	108.1	182.5

XV.—*Manganous sulphate; ethyl alcohol; water.*

1 cc. of solution containing 0.3205 gram $MnSO_4$ and 0.97 gram H_2O.

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[1] Although layers formed in mixtures of sodium sulphate, ethyl alcohol and water, as well as of sodium sulphate, acetone and water, within not very narrow bounds, it was impossible to determine these limits with any degree of accuracy, since before the cloudiness indicative of the beginning of the separation of layers set in, salt crystallised out; I am unable, therefore, to give any data. With propyl alcohol and water, however, sodium sulphate formed very well defined layers.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 3.1.	Alcohol × 3.1.
I	1.	0.04	2.01	1.3	1.	6.2	3.1
II	4.9	0.19	6.06	6.4	4.93	18.7	15.3
III	6.8	0.29	8.06	9.9	7.63	24.9	23.7
IV	11.4	0.61	12.98	19.5	15.	40.2	46.5
V	15.	0.83	16.8	28.5	22.	52.	68.2

XVI.—*Manganous sulphate; propyl alcohol; water.*

1 cc. of solution containing 0.3205 gram $MnSO_4$ and 0.97 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 3.1.	Alcohol × 3.1.
I	3.2	4.17	2.3	1.84	12.9	6.8
II	6.8	7.77	6.8	5.44	24.0	16.8
III[1]	12.8	13.77	12.8	10.24	36.7	42.7
IV	14.2	15.17	18.2	14.56	47.0	55.1

XVII.—*Manganous sulphate; acetone; water.*

1 cc. of solution containing 0.3205 gram $MnSO_4$ and 0.97 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 3.1.	Acetone × 3.1.
I	2.5	3.47	1.7	1.36	10.7	4.1
II	7.55	8.52	6.	4.8	26.4	14.8
III	12.	12.97	10.9	8.72	39.2	27.0
IV	16.2	17.17	15.8	12.64	53.2	38.1
V	22.	22.97	23.6	18.88	71.2	58.5
VI	25.1	26.07	28.	22.4	80.8	69.4
VII	31.	31.97	37.5	30.00	99.1	93.0
VIII	34.5	35.47	43.1	34.48	109.9	106.8

The results of the determinations are given graphically in Figs. I, II and III. The amount of organic liquid is measured along the axis of abscissæ, the amount of water along the axis of ordinates. The numbers are taken from the last two columns in the tables, so that the curves represent the number of parts by weight

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[1] Here a curious phenomenon presented itself. On agitating the mixture of the two layers, no turbidity ensued, but a perfectly clear solution was obtained with no trace of layers. On letting it stand for a few minutes, however, well-defined layers separated out. Hence it was difficult to detect the beginning of the disappearance of the layers. By operating as follows I was withal able to determine the point with a fair degree of accuracy. After the addition of alcohol or water, as the case might be, the bottle was allowed to stand quietly in the thermostat for an hour or so. The least trace of a layer could then be detected by tipping the bottle on its side, when the layer would appear as a streak running along the side of the bottle.

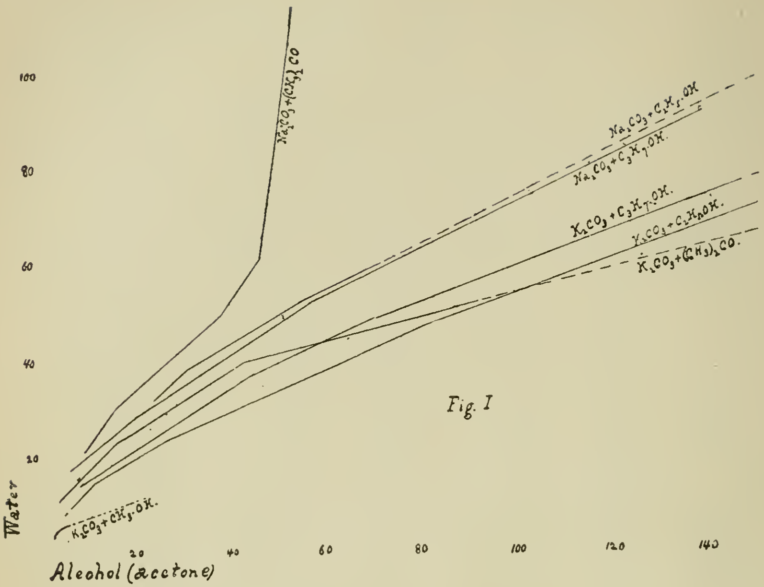
$Na_2CO_3+(CH_3)_2CO$
$Na_2CO_3+C_2H_5.OH$
$Na_2CO_3+C_3H_7.OH$
$K_2CO_3+C_3H_7.OH$
$K_2CO_3+C_2H_5OH$
$K_2CO_3+(CH_3)_2CO$
$K_2CO_3+CH_3.OH$
100
80
60
40
20
Water
20
40
60
80
100
120
140
Alcohol (acetone)

Fig. I

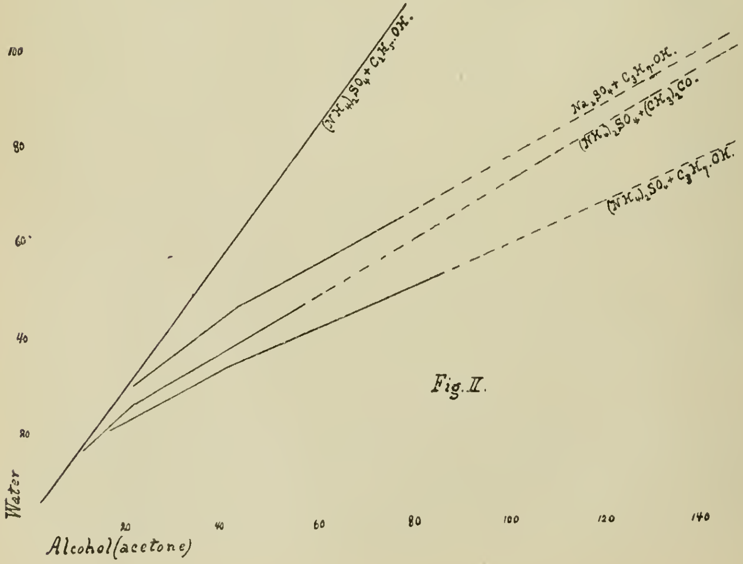
$(NH_4)_2SO_4+C_2H_5.OH$
$Na_2SO_4+C_3H_7.OH$
$(NH_4)_2SO_4+(CH_3)_2CO$
$(NH_4)_2SO_4+C_3H_7.OH$
100
80
60
40
20
Water
20
40
60
80
100
120
140
Alcohol (acetone)

Fig. II.

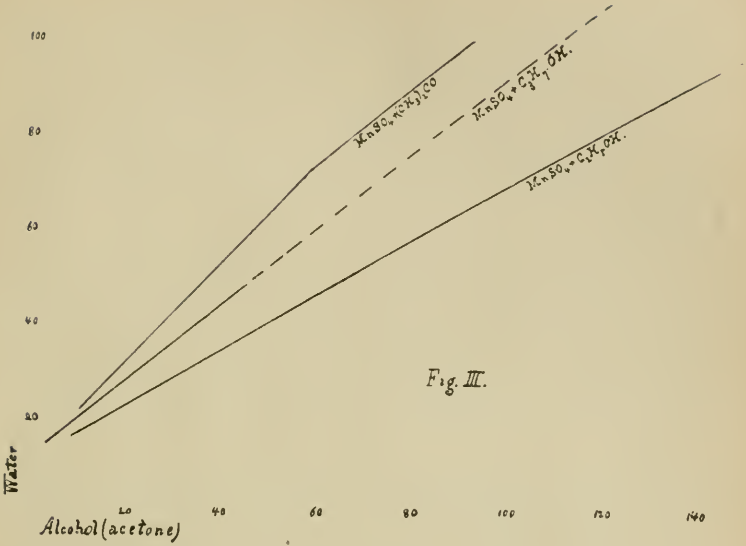

Fig. III.

of alcohol (acetone) and water present to one part of salt. The dotted portions of the curves are those which could not be determined experimentally, and are made by the continuation of the line passing through the last two points obtained. The curves have generally the same outline. They rise rapidly at first, and then gradually become more and more flattened. This means that when the amount of salt in the system is large in proportion to the quantities of organic liquid and water, the amount of water is relatively much greater than when the quantity of salt is small in proportion to the liquid constituents of the system. As the solution of the salt in the dissolving mixture becomes more dilute, the solution of the organic liquid in the water becomes more concentrated. The greater the mass of the solvent compared with the mass of the salt, the more organic liquid is present. The curves of the alkaline carbonates (Fig. I), as might be expected, are quite similar, with the exceptions of those where acetone is present. Potassium carbonate–ethyl alcohol–water and potassium carbonate–propyl alcohol–water, as well as sodium carbonate–ethyl alcohol–water, and sodium carbonate–propyl alcohol–water are quite parallel through their whole length, the curves of the sodium salt being situated higher up than those of the potassium salt.

The curves of sodium and ammonium sulphate (Fig. II) are quite similar. Sodium sulphate–propyl alcohol–water and ammonium sulphate–acetone–water lie quite close together, while ammonium sulphate–ethyl alcohol–water and ammonium sulphate–propyl alcohol–water are seen to diverge considerably. The curves for manganous sulphate (Fig. III) lie quite close together, and, as the tables show, the layers of the salt are formed within wide limits.

There is one curious fact to note concerning the curves in which propyl alcohol is found. The curve sodium sulphate–propyl alcohol–water lies almost exactly between the curves manganous sulphate–propyl alcohol–water and ammonium sulphate–propyl alcohol–water, and the molecular mass of sodium sulphate is just about the half of the sum of the molecular masses of the other two salts.

In Fig. I is given the curve for potassium carbonate–methyl alcohol–water. In comparison with the other systems in the figure, it is very short indeed. As stated in Part I, the greater the molecular mass of the alcohol in a system, the wider apart are, in general, the limits of layer-formation. Other analogies in the curves present themselves which will be more thoroughly discussed in Part III. The relations are very complicated, and it will be only by a thorough study of the composition of the layers and their physical constants that light may be obtained on the subject. I have already made numbers of determinations of the compositions of systems such as potassium carbonate–ethyl alcohol–water, sodium carbonate–ethyl alcohol–water and manganous sulphate–ethyl alcohol–water, and am waiting only until I shall have found a ready means for the analyses of propyl alcohol and acetone, to extend my investigations. I am led to believe that the study of the surface tensions will also throw some light upon the matter.

The third part of this research, together with some discussions and conclusions, I hope to have ready for publication in a few months.

CHICAGO, ILL.

REVIEWS AND REPORTS.

The Configuration of Grape-Sugar and its Isomers.

The researches of Emil Fischer upon the constitution and synthesis of sugars are well known through his numerous papers in the *Berichte*. The same have been reviewed in this Journal[1] and also in *Agricultural Science*.[2] These researches have now proceeded so far, and the results harmonise so entirely with the theory of the asymmetric carbon atom, that Fischer proposes, in two late papers,[3] to assign certain specific configurations to those of the sugars which have been well studied.

Bold as this undertaking seems, his conclusions, all based on experimental data, conform to the requirements of the theory and are ingeniously and skilfully drawn.

According to the theory there may exist sixteen isomers of the structure of grape-sugar, and for those derivatives of the same which have symmetrical molecules, *i. e.* dibasic acids and hexavalent alcohols, ten different structures are possible. These structures are expressed by the following table taken from van't Hoff-Herrmann's paper, "Die Lagerung der Atome im Raume," in which the signs + or — are used to indicate the relative arrangement of the hydrogen and hydroxyl upon the four non-terminal carbon atoms of the sugar molecule, accordingly as their sequence conforms to the direction in which the hands of a watch move, or the reverse.

				11	12	13	14	15	16
				+	+	+	+	+	—
				+	+	+	—	—	+
				+	—	—	+	—	—
				—	+	—	—	—	—
+	+	—	—	—	+	—	—	—	—
+	—	+	—	+	—	—	+	—	—
+	—	+	—	+	+	+	—	—	+
+	+	—	—	+	+	+	+	+	—
1	2	3	4	5	6	7	8	9	10

Of these it is evident that the arrangements 5–10 are identical with 11–16, so far as the alcohols or dibasic acids are concerned.

In order now to assign one of these configurations to grape-sugar upon the ground of experimental data it is necessary to consider the saccharic acid of which both optical forms are known. The d. saccharic acid is derived from both the d. and l. glucose,[1] they being stereoisomeric. Hence the two acids must be included in cases 5–10, since only such can be derived from stereoisomeric sugars. But of these numbers, 7 and 8 are optically inactive and therefore not to be considered. Of the remaining cases, numbers 6 and 10 may also be rejected on the ground of the following experimental proofs.

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[1] **11**, 277 and **12**, 357.

[2] **6**, No. 4.

[3] Ber. d. chem. Ges. **24**, 1836 and 2683.

Glucose and mannose differ from each other only in the configuration of the carbon atom, designated by an asterisk in the following formula,

$$\mathrm{CH_2OH.CHOH.CHOH.CHOH.{*}CHOH.COH,}$$

and the same, of course, holds true for their derivatives (sorbite and mannite, gluconic and mannonic acids, and saccharic and manno-saccharic acids). The proofs of this hypothesis are strong as presented by Fischer:

1. Mannose and glucose yield the same "osazon."[2]
2. Arabinose, by the addition of hydrocyanic acid, HCN, yields in the same reaction l. mannonic and l. gluconic acids.[3]
3. Fructose is reduced by sodium amalgam to a mixture of mannite and sorbite.[4]
4. Mannonic and gluconic acids, on being heated with pyridine or quinoline, are each transformed into the other.[5]
5. All attempts to separate mannonic or gluconic acids into different components have failed.[6]

Accepting these proofs of the relative structure of the above bodies, numbers 6 and 10 become impossible, for the following reasons: If saccharic acid, or what is the same thing, sorbite, had
the structure 6, + — + +,
or 10, — — + —,
then the manno-saccharic acid or the mannite would have the
structures 7, — — + +,
or 8, — + — +,
but these are both inactive combinations, while the mannite and manno-saccharic acid are both active.

There remain, therefore, for the d. and l. saccharic acids only the two configurations 5 and 9, and since it is immaterial just which arrangement of hydrogen and hydroxyl one understands by + and which by —, Fischer assigns arbitrarily the configuration 5 to d. saccharic acid,

$$\mathrm{COOH.\underset{-}{CHOH}.\underset{+}{CHOH}.\underset{+}{CHOH}.\underset{+}{CHOH}.COOH,}$$

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[1] Ber. d. chem. Ges. **24**, 521.
[2] **22**, 374.
[3] **23**, 2611.
[4] **23**, 3684.
[5] **23**, 800.
[6] **23**, 800.

and 9 to the l. saccharic acid,

$$\mathrm{COOH.\underset{+}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.COOH.}$$

But corresponding to the d. saccharic acid are two aldehyde sugars, d. glucose, or grape-sugar, and the d. gulose, a synthetic product. These, being stereoisomeric, would have the configurations,

$$\mathrm{5.\ COH.\underset{-}{CHOH}.\underset{+}{CHOH}.\underset{+}{CHOH}.\underset{+}{CHOH}.CH_2OH}$$

and

$$\mathrm{11.\ COH.\underset{+}{CHOH}.\underset{+}{CHOH}.\underset{+}{CHOH}.\underset{-}{CHOH}.CH_2OH.}$$

In order to assign one of these definitely to grape-sugar and the other to d. gulose it is necessary to again extend our observations to another series of sugars, viz. the pentoses.

From one of these, arabinose, is derived l. glucose, and from the other,[10] xylose, comes l. gulose. For these latter (l. glucose and l. gulose) there remain the configurations 9 and 15,

$$\mathrm{COH.\underset{-}{{}^{*}CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{+}{CHOH}.CH_2OH}$$

and

$$\mathrm{COH.\underset{+}{{}^{*}CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.CH_2OH.}$$

In these formulas the asymmetric carbon atoms designated by the asterisk have been created by synthesis and do not exist in arabinose and xylose. Rejecting them, we have as the possible configurations of the two pentoses,

$$\mathrm{COH.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.CH_2OH}$$

and

$$\mathrm{COH.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{+}{CHOH}.CH_2OH.}$$

For the pentoses of the structure of arabinose and xylose (aldehydes) there are eight possible isomers, or for the corresponding dibasic acids or alcohols the number is four, of which two are active and two inactive systems. The theoretical configurations of the two active forms of the dibasic acids are as follows:

$$\mathrm{COOH.\underset{+}{CHOH}.\underset{+}{CHOH}.\underset{+}{CHOH}.COOH}$$

$$\mathrm{COOH.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.COOH,}$$

and of the inactive forms:

$$\mathrm{COOH.\underset{+}{CHOH}.\underset{+}{CHOH}.\underset{-}{CHOH}.COOH}$$

$$\mathrm{COOH.\underset{+}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.COOH.}$$

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[10] Ber. d. chem. Ges. **24**, 529.

The optical behavior of the acids or alcohols derived from arabinose and xylose would therefore serve to indicate in which of the above couples their configuration belongs. Here again the experimental testimony is clear, for both the arabite (upon the addition of borax) and the trioxy-glutaric acid from arabinose showed laevo-rotation. Arabinose, therefore, belongs to one of the two active systems, preferably the second, and its configuration would be as follows:

$$\mathrm{COH.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{-}{CHOH}.CH_2OH.}$$

The xylose on the other hand belongs to the inactive systems, since the xylite, even with borax, and the trioxy-glutaric acid from xylose, are both without influence upon polarised light. To the xylose therefore is assigned this configuration:

$$\mathrm{COH.\underset{-}{CHOH}.\underset{-}{CHOH}.\underset{+}{CHOH}.CH_2OH.}$$

The configurations thus experimentally indicated for these sugars would of course hold for their derivatives among the hexoses, viz. the l. glucose and l. gulose, and from these the configurations of other members of the group are easily deduced, as follows:

Hexose Sugars.

Aldoses.	COH.	CHOH.	CHOH.	CHOH.	CHOH.	$\mathrm{CH_2OH}$
d. glucose,		−	+	+	+	
l. glucose,		+	−	−	−	
d. gulose,		+	+	+	−	
l. gulose,		−	−	−	+	
d. mannose,		+	+	+	+	
l. mannose,		−	−	−	−	

(For galactose the experimental data do not yet justify a choice between the four possible configurations indicated by a study of the mucic and allomucic acids.)

Ketoses.	COH.	CO.	CHOH.	CHOH.	CHOH.	$\mathrm{CH_2OH}$.
d. fructose,			+	+	+	
l. fructose,			−	−	−	

The mono- and di-basic acids and hexavalent alcohols derived from these sugars retain their respective configurations, and we have therefore reasonable experimental proof of the configuration of upwards of twenty bodies which are either sugars or closely related to them.

Fischer takes good care to remark, however, that these conclusions can only stand provided the theory of the asymmetric carbon atom is wholly in accord with the facts, and provided the oxidation of arabinose and xylose to the respective trioxy-glutaric acids occurs without intramolecular changes.

In the expressions used above, however, the signs + and — may easily be misinterpreted, and to prevent confusion, Fischer in a second paper presents these configurations in a clearer manner. Taking the familiar models of the carbon atoms and constructing the sugar molecules according to the configurations proposed above, he develops graphic formulæ which have a new significance and permit an easy comparison of the different sugar molecules.

The four asymmetric carbon atoms may be designated by numbers as follows:

$$CH_2OH.\overset{1}{C}HOH.\overset{2}{C}HOH.\overset{3}{C}HOH.\overset{4}{C}HOH.COH.$$

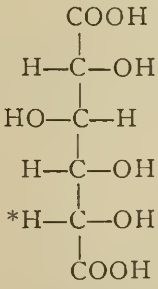
In the discussion of van't Hoff, upon which Fischer's deductions are based, the carbon atom 1 is compared only with 4, and 2 with 3. Consequently, in the configuration assigned to d. glucose or grape-sugar,

$$CH_2OH.\underset{+}{\overset{1}{C}HOH}.\underset{+}{\overset{2}{C}HOH}.\underset{+}{\overset{3}{C}HOH}.\underset{-}{\overset{4}{C}HOH}.COH,$$

the arrangement of hydrogen and hydroxyl upon 1 is the opposite of that upon 4, while 2 and 3 are alike. If 1 be compared with 3 it is found that the arrangement is also the same. From a superficial examination the same would seem to follow for 1 and 2, but this is not the case, for the sign of 2 changes accordingly as it is compared with 3 or 1, as is apparent from the study of the model.

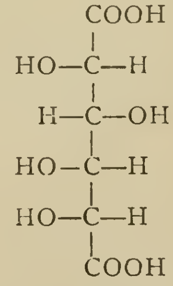
That is, the above expression for the configuration of grape-sugar permits of two interpretations, and to avoid confusion the structure is represented graphically as follows: By means of the flexible rubber models the molecules of the d. and l. saccharic acids are constructed; these are then placed upon a plane surface in such way that the carbon atoms lie in a straight line, when the hydrogens and hydroxyls arrange themselves on either side, and by projection present the following arrangements:

I.



$$\begin{array}{c} COOH \\ | \\ H—C—OH \\ | \\ HO—C—H \\ | \\ H—C—OH \\ | \\ {}^{*}H—C—OH \\ | \\ COOH \end{array}$$

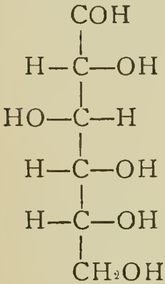
II.



$$\begin{array}{c} COOH \\ | \\ HO—C—H \\ | \\ H—C—OH \\ | \\ HO—C—H \\ | \\ HO—C—H \\ | \\ COOH \end{array}$$

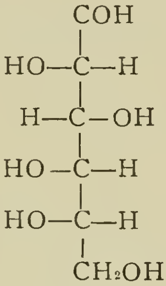
The same appearance is also obtained by the use of the inflexible wire models, arranging the carbon atoms in a vertical plane and regarding the structure from above. Fischer selects the first from the two above expressions for the d. saccharic acid, whereby it is again immaterial if, at starting, the arrangement of hydrogen and hydroxyl upon the starred carbon atom does or does not follow the motion of the hands of a watch. From this, therefore, are derived the following graphic representations of the configurations of the d. glucose and its isomers, the same being projections of models constructed on the basis of the configurations already indicated by the + or — signs.

Of course these projection formulas have a quite different significance from others of similar *appearance* which have been proposed before.



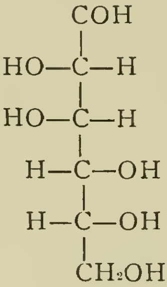
$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Grape-sugar.



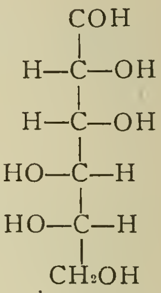
$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

l. glucose.



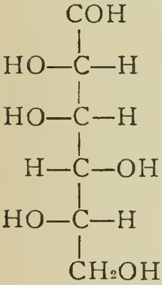
$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

d. mannose.



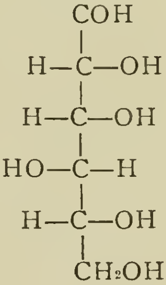
$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

l. mannose.



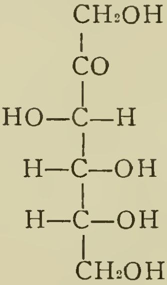
$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

d. gulose.



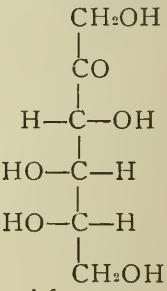
$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

l. gulose.



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

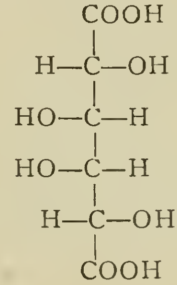
d. fructose.



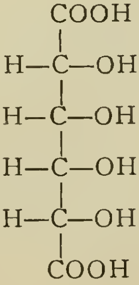
$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

l. fructose.

The projections for the two inactive dibasic acids of the dulcit series, which probably exist as the mucic and allomucic acids, are also given, as possibly furnishing some insight into the configuration of the galactose.

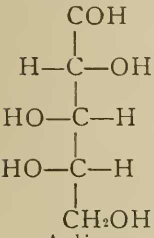


$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{COOH} \end{array}$$



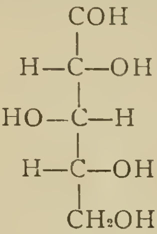
$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{COOH} \end{array}$$

In the same way the following projections for the pentoses and their corresponding trioxy-glutaric acids are obtained:



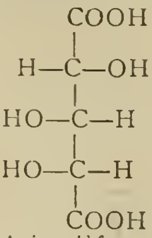
$$\begin{array}{c}\mathrm{COH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Arabinose.



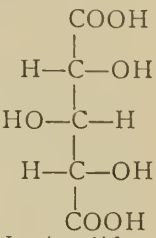
$$\begin{array}{c}\mathrm{COH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Xylose.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{COOH}\end{array}$$

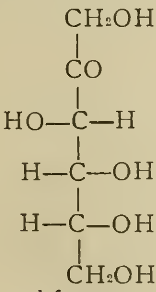
Active acid from Arabinose.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{COOH}\end{array}$$

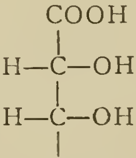
Inactive acid from Xylose.

Working from these formulas, the models of the molecules are easily constructed in which the + or — arrangement of each asymmetric carbon atom is readily seen. Their value is also apparent in the study of such reactions as increase or decrease the number of asymmetric carbon atoms, as an example of which the oxidation of fruit-sugar or levulose to inactive tartaric acid is given. The comparison of the projection formulas of the two bodies renders it apparent how this reaction is possible.



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{HO-C-H}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d. fructose.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{COOH}\end{array}$$

Inactive tartaric acid.

Undoubtedly this insight thus obtained into the constitution and configuration of the sugars will point out the way to new reactions and to new explanations of known reactions; and in any event, Fischer's work, of which these last papers present the climax, constitutes the most notable contribution yet made to the subject.

PURDUE UNIVERSITY, *April*, 1892. W. E. STONE.

CONSTITUTION OF BENZENE.[1]

In the last communication by von Baev
the following passage occurs:

"The task which I set myself at th
gations was to determine the con

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[1] Annalen der (

mental methods, and not to prove the correctness of any hypothesis by experiment. Accordingly, I have changed my view repeatedly, as the sum of my experiences has seemed to speak more for one view or the other. If now I put prominently forward an hypothesis which I formerly opposed, I beg the reader not to be surprised, and not to accuse me of inconsistency, if later I should prefer another hypothesis."

"The hypothesis I refer to is that of Claus. It consists in the assumption that each carbon atom of benzene is united to the two adjoining atoms by ordinary single union, and to the carbon atom in the para position by a peculiar bond. I objected to this hypothesis mainly because such para-bonds could not be found in the reduction-products of the benzene-carbonic acids, and I therefore put forward the centric formula, which is intended to express the idea that the diagonal valencies of Claus are not united with each other, but are free and directed towards the center. I observed, however, that this formula is identical with that of Claus if in the case of the latter it be assumed that the rupture of a single para-bond caused both the others to go over into double bonds."

"I shall now, on the basis of new facts, attempt to prove that the formula of Claus agrees best with the facts, with this limitation, that para-bonds exist only as long as the benzene-nucleus remains intact." The author then shows that:

1. No conclusion as to the constitution of benzene can be drawn from the course of the reduction of a benzene-derivative; and
2. The reformation of a benzene-nucleus from a hydro-derivative can throw light upon the constitution of benzene.

And says: "The question as to the constitution of benzene is, however, not yet fully answered, because Claus' formula gives a definite picture of the structure of the benzene-molecule, only in case we assume that the carbon atoms of the molecule lie in a plane, and that the four valencies of each of these atoms correspond even in this condition to the four angles of a regular tetrahedron. . . . The material now available is, however, still too meager to lead to a definite conception of the space configuration of the benzene molecule. I consider, therefore, the solution of this stereochemical problem as the task that should next be undertaken, and I have begun the investigation of the reduction-[illegible] of isophthalic acid as well as of the carbonic acids of [illegible] compounds." I. R.

VOL. XIV. [OCTOBER, 1892.] NO. 6.

AMERICAN

CHEMICAL JOURNAL.

Contribution from the Laboratory of General Chemistry, University of Michigan.

SOME REACTIONS WITH ACETOACETIC ETHER AND WITH SALICYLIC ETHER.

BY PAUL C. FREER.

In a paper published by me last year[1] I gave a number of reasons why, in my opinion, acetoacetic ether is to be regarded as the ester of β-ketobutyric acid, while the sodium salt of this same substance is the derivative of β-hydroxycrotonic ether. Since that time J. U. Nef,[2] in an exhaustive paper, rich in experimental facts, has concluded that the only interpretation of the evidence which he has accumulated is that under all circumstances, whether as the free acid or in its metallic derivatives, acetoacetic ether behaves as if it were an unsaturated β-hydroxy ester. Von Pechmann,[3] in discussing some reactions of formylacetic ether, demonstrated that the latter substance is β-oxyacrylic ether, $CHOH = CH - COOC_2H_5$, and, owing to the radically different behavior of β-oxyacrylic ether and its derivatives toward acetyl chloride, benzoyl chloride, and toward aniline, concludes that acetoacetic ether undoubtedly has the ketone formula. More recently Claisen[4] published a paper on the action of chlorcarbonic ester on sodium acetoacetic ether. In this he enters into an extended discussion of the same reaction which was studied by Nef, and comes to conclusions which differ from those of the latter author. I would, myself, scarcely venture to resume the discussion of this extremely voluminous subject, did it not seem to me that I can advance further experimental evidence to disprove one or two of the conclusions reached by Prof. Nef in his previous article. On page 58 of Nef's paper the statement appears that, "provided a direct exchange of sodium and bromine respectively alkyle takes place when halogenes, acid chlorides or alkylhalides react with sodium acetoacetic ether, then the corresponding reactions must take place much more energetically with the salts of the heavy metals such as copper, lead and mercury acetoacetic ether," and the author concludes from the facts that the sodium derivative of acetoacetic ether reacts with alkyl halides, bromine, and with acid chlorides in the cold, and with the greatest energy, while, for instance, the copper and lead salts do so only very slowly when heated with a solvent in sealed tubes at 130°, that an addition of the reagents in question to the sodium derivative takes place previous to the separation of the sodium halide. In order to discover whether phenomena similar to those observed with sodium acetoacetic ether take place with substances with which no such additive action is possible, I investigated the reactions of sodium salicylic ester. The latter substance and acetoacetic ether, provided the latter is β-hydroxycrotonic ether, are similarly constituted,[1] as a glance at the following formulæ will show:

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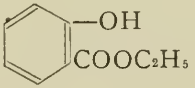
[1] This Journal **13**, 309.

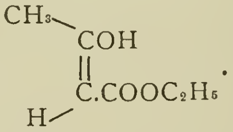
[2] Ann. Chem. (Liebig) **266**, 52.

[3] Ber. d. chem. Ges. **25**, 1044.

[4] Ber. d. chem. Ges. **25**, 1760.



and



Now, sodium salicylic ether reacts readily, in the cold, with benzoyl chloride, and does so with ethyl or methyl iodide when in alcoholic solution and slightly warmed on the water-bath, yet, in each of these cases, the substituting radicle is bound to oxygen, as is proven by the readiness with which it is split off by saponifying agents, so that the theory of addition is excluded in this case; furthermore, copper salicylic ether does not react at all under similar circumstances. Sodium salicylic ether in its physical characteristics is wonderfully similar to sodium acetoacetic ether.

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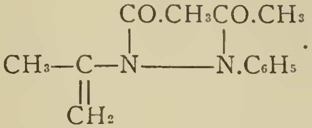
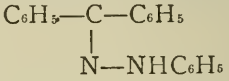
[1] Claisen, Ber. d. chem. Ges. 25, 1780, also calls attention to this similarity. My work was completed previous to the publication of Claisen's article. The latter, however, publishes no experimental work on this point.

One of the chief reasons advanced by Nef in support of the theory that acetoacetic ether is β-hydroxycrotonic ether is the formation of β-phenylhydrazocrotonic ether by the action of phenylhydrazine on the former. The proofs advanced as to the constitution of this substance are, that it is readily oxidised to β-phenylazocrotonic ether by mercuric oxide, and that, when treated with acetyl chloride, it forms a substance which Nef regards as having the structure:



$$\begin{array}{llll} & & \text{CO.CH}_3 & \text{CO.CH}_3 \\ & & | & | \\ \text{CH}_3\text{—} & \text{C—} & \text{N————} & \text{N.C}_6\text{H}_5 \\ & \| & & \\ & \text{CH}_2 & & \end{array}.$$

In studying the action of phenylhydrazine hydrochloride on acetoacetic ether I discovered that, in addition to 1-phenyl, 3-methyl, 5-pyrazolon, a substance melting at 36° is produced. The latter reacts readily when heated with methyl iodide, producing a thick syrup which, like antipyrin, is perfectly soluble in water. From this it follows, that at least one of the hydrogen atoms, which were attached to nitrogen in phenylhydrazine, is still present in the body melting at 36°. As I suspected that the oil which Nef obtained by the action of acetyl chloride on β-hydrazocrotonic ether might be identical with my low-melting solid, I repeated Nef's experiment and found that when β-hydrazocrotonic ether is treated with an excess of acetyl chloride, phenylmethylpyrazolon (which Nef overlooked), and an oil having the same boiling-point as that given by Nef, and identical with the boiling-point of my 36° melting solid, are produced. After repeated fractioning I obtained this oil in a solid form, it then melted at 36°, and was identical with the substance obtained by me from the action of phenylhydrazine hydrochloride on acetoacetic ether. The analysis of the pure substance, as well as the fact that it readily reacts with methyl iodide to form a body which is soluble in water, leaves no doubt that the formula assigned by Nef is incorrect. Although this experimental proof of the theory that the first product of the action of phenylhydrazine on acetoacetic ether is β-hydrazocrotonic ether is proven to be wrong, yet I have no doubt that the formula assigned to that substance by Nef is the correct one, from the following reasons. The phenylhydrazine derivatives of acetone and of acetophenone—two cases where the substances in question may have the formulæ $CH_3.COH = CH_2$ and $C_6H_5.COH = CH_2$,—are extremely unstable, when exposed to the air they are most readily oxidised, while benzoyl chloride, acetyl chloride, benzoic aldehyde, etc., readily decompose them in the cold. If benzoyl chloride is the reagent used, they separate phenylhydrazine hydrochloride, respectively dibenzoyl phenylhydrazine; on the other hand, the solid obtained by the action of phenylhydrazine on benzophenone, which is necessarily a hydrazone:  $\begin{array}{c} C_6H_5—C—C_6H_5 \\ | \\ N—NHC_6H_5 \end{array}$ is quite unchanged when exposed to the air and is not decomposed by benzoyl chloride.[1]

If acetoacetic ether is β-hydroxycrotonic ether, $CH_3.COH:CH.COOC_2H_5$, it should be capable of adding hydrobromic acid to form a tolerably stable addition-product; for aconitic acid, in which the carboxyl group, instead of hydroxyl, is attached to the β-carbon atom, reacts with hydrobromic acid to form bromtricarballylic acid. If acetoacetic ether, in ethereal solution, is treated with hydrobromic acid, even if the mixture is cooled with snow and salt, decomposition and the formation of carbacetoacetic ether takes place. On the other hand, if the ether is treated with exactly the calculated quantity of dry gaseous hydrobromic acid, a heavy oil is formed and the latter does not lose all of its halogen, even when repeatedly shaken with water, the product, after several washings, contains at least 10 to 12 per cent. of bromine; the latter is, however, completely removed by alcoholic potash and acetoacetic ether is regenerated. This hydrobromic acid addition-product, if it be such, is, however, extremely unstable. When allowed to stand, it decomposes, the liquid becomes dark in color and the usual decomposition-products of acetoacetic ether are formed. When treated with zinc ethyl no substances are formed, so far as I could discover, except high-boiling decomposition-products and regenerated acetoacetic ether. From these facts I am inclined to the opinion that this body is not a true hydrobromic addition-product in which hydrogen is attached to one carbon atom and bromine to the other. Were acetoacetic ether to have the ketone formula it is conceivable that hydrobromic acid could add as follows:

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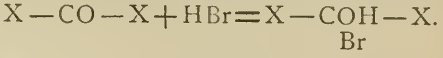
[1] The phenylhydrazide of acetone is readily oxidised by mercuric oxide, forming a deep red oil, from which, however, it has been impossible to separate a pure product, the hydrazone of benzophenone is very slowly attacked by mercuric oxide. Mr. Lichty is undertaking a study of these reactions in this laboratory.



$X-CO-X+HBr=X-\underset{Br}{COH}-X.$

Such a body would, however, lose hydrobromic acid with the greatest ease.

One argument which has been repeatedly advanced against the hydroxyl formula of acetoacetic ether is that the latter substance does not react with acetyl chloride. I thought it of interest to study the action of the similarly constituted salicylic ether toward the same reagent, and found that it readily yielded acetyl salicylic ether. As yet, none of the advocates of the hydroxy formula of acetoacetic ether has explained why the hydroxyl group in that substance will not yield an acetyl derivative when treated with acetyl chloride; to my mind it should do so at least as readily as salicylic ether.

EXPERIMENTAL PART.

Sodium salicylic ether.—When salicylic ether is treated with metallic sodium, reaction at once sets in and the substance soon solidifies.[1] A better method for preparing this body is to dilute pure salicylic ether with about five times its own volume of dry toluene, and then to add sodium, which has been finely powdered under boiling toluene. The little pieces of sodium become covered with a layer of sodium salicylic ether, which prevents further action. The latter is very difficult to remove even by violent shaking of the flask, so that it is better not to wait for the end of the reaction, but to filter off the flaky sodium salicylic ether, dry on a porous plate, and separate the remaining pieces of sodium by means of a fine sieve. If salicylic ether is dissolved in a large quantity of dry ether, a concentrated solution of caustic soda then added, and the flask violently shaken, the sodium derivative will, after a little time, separate as an asbestos-like mass, which gradually, when dried, assumes a crystalline structure.

Sodium salicylic ether is a white solid which, when exposed to the air, has a pronounced odor of salicylic ether, due to the decomposition of the salt by moisture. Its solution in water has a strongly alkaline reaction and is partially decomposed with the separation of oily particles of salicylic ether. On addition of acids, unchanged salicylic ether separates from its sodium derivative.

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[1] Schreiner, Ann. Chem. (Liebig) **197**, 19.

0.7534 gram $C_9H_9O_3Na$ gave 0.2668 gram Na_2SO_4.

	Calculated for $C_9H_9O_3Na$.	Found.
Na	12.2 per cent.	11.5 per cent.

When sodium salicylic ether is suspended in dry chloroform and dry bromine is then added, reaction, accompanied by the separation of sodium bromide, at once sets in. The addition of bromine is continued until a permanent bromine color remains; the sodium chloride is then filtered and the clear chloroform solution evaporated. There remains a thick oil, which, however, soon becomes permeated with a mass of large, shiny crystals. After no more change takes place, the latter are filtered and recrystallised from dilute alcohol. The filtrate is unchanged salicylic ether, while the crystals, which are formed in a lesser quantity, consist of a dibrom-substitution-product of the latter. The formation of the free ether demonstrates that the bromine, when added, does not attack the sodium, but on the contrary takes the place of hydrogen, and that the hydrobromic acid so formed decomposes sodium salicylic ether, forming sodium bromide and salicylic ether.

1. $C_6H_4COOC_2H_5ONa + 4Br = C_6H_2Br_2COOC_2H_5ONa + 2HBr$.

2. $2C_6H_4COOC_2H_5ONa + 2HBr = 2C_6H_4COOC_2H_5OH + 2NaBr$.

This observation is entirely in accord with Nef's theory as to the action of bromine on sodium acetoacetic ether, that author believing that in the latter case addition of bromine first takes place, that this is followed by a separation of hydrobromic acid, and that the latter in turn forms sodium bromide and free acetoacetic ether. As a consequence this observation certainly supports the theory of the oxycrotonic ether formula for the sodium salt of acetoacetic ether

Dibromsalicylic ether.—Dibromsalicylic ether, formed as indicated above, crystallises from dilute alcohol in beautiful, shiny plates which have the appearance of mother-of-pearl. The substance dissolves in potassium hydroxide, and is separated therefrom unchanged by the addition of acids; it is even dissolved by a hot solution of sodium carbonate. The substance is with difficulty soluble either in cold or in hot water. When pure it melts at 100° to 101°.

0.1988 gram $C_9H_8Br_2O_3$ gave 0.2456 gram CO_2 and 0.0469 gram H_2O.

0.3196 gram $C_9H_8Br_2O_3$ gave 0.3709 gram AgBr.

	Calculated for $C_9H_8Br_2O_3$.	Found.
C	33.33 per cent.	33.69 per cent.
H	2.47	2.62
Br	49.53	49.37

When dibromsalicylic ether is heated with an excess of alcoholic potash on a water-bath for some hours it is completely saponified; when, after evaporating the alcohol and filtering, an excess of dilute sulphuric acid is added, dibromsalicylic acid separates as a white solid. This dibromsalicylic acid crystallises from dilute alcohol in white needles which melt at 225°, and is probably identical with the *m*-*m*-dibromsalicylic acid obtained by Lellmann and Grothmann.[1]

0.1558 gram $C_7H_4Br_2O_3$ gave 0.1997 gram AgBr.

	Calculated for $C_7H_4Br_2O_3$.	Found.
Br	54.05 per cent.	54.54 per cent.

Dibromsalicylic ether is changed to salicylic acid when treated for some time, in boiling dilute alcoholic solution, with an excess of sodium amalgam. Zinc dust and acetic acid have no effect, even when boiling.

The action of bromine on free salicylic ether results in the formation, not of a dibrom-, but of a monobrom substitution-product. If pure salicylic ether is dissolved in dry chloroform, and dry bromine, free from hydrobromic acid, is added, reaction begins slowly, and gradually increases in rapidity, although it at no time becomes violent. After an excess of bromine has been used and the evolution of hydrobromic acid has ceased, which takes place at the end of about twenty-four hours, the chloroform is distilled; the remaining oil, on cooling, crystallises in long needles which, after recrystallisation from nearly absolute alcohol, melt at 49° to 50°.

0.1814 gram substance gave 0.1394 gram AgBr.

	Calculated for $C_9H_{10}O_3Br$.	Found.
Br	32.4 per cent.	32.69 per cent.

Monobromsalicylic ether was saponified with alcoholic potash by heating on a water-bath for two hours; the alcohol was then distilled and the whole acidified. A white solid separates which, upon recrystallisation from dilute alcohol, forms colorless needles having a melting-point of 165° to 166°.

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[1] Ber. d. chem. Ges. **17**, 2728.

0.1852 gram substance gave 0.1627 gram AgBr.

	Calculated for $C_7H_5BrO_3$.	Found.
Br	36.86	37.5

This substance is undoubtedly the *m*-bromsalicylic acid obtained by Hübner and Heinzerling[1] by the action of bromine on free salicylic acid. The formation of the *m*-bromsalicylic ether by the action of bromine on salicylic ether seems, to my mind, to be an additional proof that at least one of the bromine atoms in the dibrom ether is in the meta position to carboxyl; but the reason why bromine forms a dibrom and not a monobrom ether, when it acts on the sodium derivative of salicylic ether, is not very apparent, although, possibly, the following explanation is the correct one. When bromine first acts on sodium salicylic ether it forms sodium monobromsalicylic ether and hydrobromic acid. The latter, however, instead of decomposing the former, attacks sodium salicylic ether to form free salicylic ether and sodium bromide. The bromine is now at liberty to once more substitute in the sodium derivative of the monobrom ether, converting the latter into sodium dibromsalicylic ether. According to this explanation, however, we would expect some monobromsalicylic ether to be formed during each reaction, but as yet I have not been able to discover such a body in the products produced.

Benzoylsalicylic ether.—If dry sodium salicylic ether is placed in a flask and covered with an excess of benzoyl chloride, reaction easily sets in in the cold and sodium chloride separates. The contents of the flask, after water has been added, are extracted with ether, the ethereal solution washed with sodium hydroxide solution, dried over calcium chloride, and evaporated. A white, crystalline solid remains which, after recrystallisation from dilute alcohol, forms small, flaky plates having a melting-point of 79° to 80°.

0.2225 gram substance gave 0.5780 CO_2 and 0.1071 H_2O.

	Calculated for $C_{16}H_{14}O_4$.	Found.
C	71.1	70.83
H	5.15	5.34

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[1] Zeitschrift für Chemie, 1871, 709.

Benzoylsalicylic ether is readily saponified when warmed for two hours with alcoholic potash. After evaporating the alcohol the whole is acidified and recrystallised from tolerably concentrated alcohol. By this means long needles separate; the latter melt at 156° and consist of salicylic acid. After filtering these crystals off the remainder is evaporated to dryness and then heated to boiling for about one hour, all of the salicylic acid being converted into phenol by this means. The decomposition-products which remain are extracted with sodium carbonate, the unchanged phenol separated by means of a wet filter, and the sodium carbonate solution acidified. A white crystalline solid precipitated, which, on recrystallisation, proved to be benzoic acid. Benzoylsalicylic ether is therefore decomposed into benzoic and salicylic acids by alcoholic potash; the benzoyl radicle is as a consequence undoubtedly attached to oxygen in this case, so that no addition-product could have been produced previous to the formation of benzoylsalicylic ether and yet *the reaction takes place readily and in the cold.*

The Action of Ethyl and Methyl Iodides on Sodium Salicylic Ether.

If dry ethyl iodide is added to perfectly dry sodium salicylic ether no reaction takes place, even on warming upon the water-bath. If, however, alcohol, in which substance sodium salicylic ether is soluble, is added, diethyl salicylic ether can readily be formed by gently heating for one or two hours, a method which is exactly like that employed in the production of alkylated derivatives of acetoacetic ether. After sodium salicylic ether in alcoholic solution has been boiled with ethyl iodide until a sample taken out and mixed with water no longer displays an alkaline reaction, the excess of alcohol and ethyl iodide is distilled, and the remainder, after the addition of water, is extracted with ether. After drying over calcium chloride the ether is evaporated, and the yellow-colored oil which remains is purified by fractional distillation. The diethyl salicylic ether so formed is a highly refracting, colorless oil which boils at 252°.[1] When boiled with alcoholic potash for two hours this substance is saponified, an oil separating on addition of acids. This oil when fractioned *in vacuo* boils at 228°, 110 mm. pressure, and when pure is a colorless, very highly refracting liquid. That this substance is in reality the ethyl ether acid is proven by the fact that it is readily hydrolised when heated in a sealed tube with concentrated hydrochloric acid, the product of this saponification being salicylic acid. An analysis of the ether-acid was not deemed necessary because of the similar reaction with methyl iodide; the methyl ether acid being a crystalline solid easily identified.

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[1] The boiling-point given by Fölsing, who prepared this substance from salicylic ethyl ether acid, is 251°.

The reaction with methyl iodide is like that with ethyl iodide; the ethylic salt of salicylic methyl ether acid being produced. This, when saponified by means of alcoholic potash, yields the potassium salt of the methyl ether acid, and the latter produces the free ether-acid when acidified. The acid crystallises from alcohol in large, transparent rods which melt at 98.5°, agreeing entirely with the descriptions of this substance previously given.[1] This methyl-ether acid is hydrolised with the greatest readiness by means of concentrated hydrochloric acid. Both methyl and ethyl iodide, therefore, with sodium salicylic ether, produce ethers in which the alkyl radicle is attached to oxygen; no addition could therefore have taken place, and yet the reaction is brought about with the greatest readiness.

In order, finally, to determine whether the compounds of the heavy metals with salicylic ether would react readily with alkyl iodides, copper salicylic ether was prepared and tested. Copper salicylic ether is easily formed by adding a solution of copper acetate to an alcoholic solution of sodium salicylic ether; it then separates as a green precipitate which can be filtered and dried. On addition of acids it regenerates salicylic ether. Now, copper salicylic ether shows no reaction with ethyl or methyl iodide even when boiled with the latter in the presence of alcohol, in which substance copper salicylic ether is slightly soluble. From these reactions it follows that the metallic derivatives of salicylic ether behave toward alkyl iodides exactly as do the similar ones of acetoacetic ether, so that in this case the supposed formation of intermediate addition-products cannot be advanced as an explanation of the ease with which sodium acetoacetic ether reacts with alkyl halides, while the salts of the heavy metals do not do so.

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[1] Graebe, Ann. Chem. (Liebig) **139**, 137, prepared the methyl ether acid and accurately described the same, as well as the ethyl ether of that body.

Acetyl salicylic ether.—Unlike acetoacetic ether, salicylic ether reacts with acetyl chloride. The ether is placed in a flask fitted with an inverted condenser, the upper extremity of which is closed by a mercury valve, a large excess of pure acetyl chloride added, and the whole boiled for some hours on a water-bath. The liquid is then poured into ice-water and extracted with ether. The ethereal solution is then repeatedly shaken with a tolerably concentrated solution of caustic soda, by which means any unchanged salicylic ether is separated, and it is then finally dried over calcium chloride. After evaporating the ether a thick oil remains, which is purified by fractional distillation. Acetyl salicylic ether boils at 272° and is very nearly colorless when pure.

0.2312 gram substance gave 0.5325 gram CO_2 and 0.1230 gram H_2O.

	Calculated for $C_{11}H_{12}O_4$.	Found.
C	62.80 per cent.	63.46 per cent.
H	5.77	5.90

Alcoholic potash very readily saponifies acetyl salicylic ether and forms salicylic acid.

The Action of Phenylhydrazine Hydrochloride on Acetoacetic Ether.

If a weighed quantity of acetoacetic ether is dissolved in alcohol and an equimolecular amount of phenylhydrazine hydrochloride is then added, reaction takes place slowly, in the same measure as phenylhydrazine hydrochloride is dissolved. After standing for twelve hours the change is complete. In order to isolate the products formed, the whole is poured into water and then repeatedly extracted with ether. This ethereal extract is washed, at first with water and finally several times with a dilute solution of sodium hydroxide. It is then dried over calcium chloride. After filtering, and evaporating the ether, an oil remains, which is best purified by repeated fractioning under diminished pressure. A small quantity which boils at 132° under ordinary barometric pressure has proved to be mesityl oxide. By far the larger portion,[1] however, boils at 202°, 32 mm. When this latter substance is cooled by means of snow and salt it solidifies. The solid so formed was purified by repeated solution in ice-cold absolute alcohol and precipitation by means of ice-water. It is then found to be a white, sandy, crystalline body which melts at 36° and which gives the following numbers on analysis:[1]

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[1] 7 grams for every 26 grams of acetoacetic ether and 28.8 grams of phenylhydrazine hydrochloride.

I. 0.1470 gram substance gave 0.3871 CO_2 and 0.1003 H_2O.
II. 0.1318 gram substance gave 0.3467 CO_2 and 0.0861 H_2O.
III. 0.1738 gram substance gave 0.4596 CO_2 and 0.1100 H_2O.
IV. 0.1815 gram substance gave 24.6 cc. N at 22° and 740 mm.
V. 0.1449 gram substance gave 19.8 cc. N at 21° and 730.5 mm.

	Found.				
	I.	II.	III.	IV.	V.
C	71.83	71.72	72.17	...	...
H	7.40	7.24	7.03	...	...
N	...	...	...	15.22	15.4

The substance used for analysis III was purified by conversion into the hydrochloride, recrystallising, liberating the base with pure potash, and once more recrystallising the latter.

The analytical data agree best with a formula of $C_{12}H_{14}N_2O$ which would require:

C	71.60 per cent.
H	6.99
N	14.

However, the nitrogen determinations give too high a result for such a substance, which would be phenylmethyl pyrazolon ($C_{10}H_{10}N_2O$) with an addition of C_2H_4. In order to throw some more light on the possible composition of this body, I prepared the hydrochloride by dissolving the solid melting at 36° in pure dry ether and then passing in dry hydrochloric acid. The hydrochloride separates as an oil, which rapidly becomes solid on rubbing with a glass rod and exposing to the air. The salt so obtained was dried over calcium oxide in a vacuum desiccator and gave the following results on analysis:

I. 0.3044 gram substance gave 0.1883 gram AgCl.
II. 0.3173 gram substance gave 0.1982 gram AgCl.

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[1] In a preliminary notice published by me (Journal für praktische Chemie **45**, 414) I gave an average of five analyses as follows: C, 69.41 per cent.; H, 6.55 per cent.; N, 15.32 per cent. As a result of these I made the statement that the oil was possibly an isomer of phenylmethyl pyrazolon. Since that time I have succeeded in crystallising this substance and, as will be seen above, the figures no longer agree with any such theory.

	Calculated for $C_{12}H_{14}N_2O.HCl$.	Found. I.	II.
Cl	14.89	15.34	15.4

So far then as the present analyses indicate, the substance melting at 36° is nearest in composition to $C_{12}H_{14}N_2O$, and, although future investigation may show this body to be a mixture, I shall, for convenience, in the remainder of this paper designate it by that formula. One thing is certain, it has not the percentage composition of the diacetyl derivative of the phenylhydrazide of acetone, the formula assigned to the oil obtained by Nef by the action of acetyl chloride on β-phenylhydrazocrotonic ether, which oil I have obtained as a crystalline solid identical with the body melting at 36°, described above.

The substance $C_{12}H_{14}N_2O$ is a white, crystalline solid which is readily soluble in alcohol, chloroform and ether, insoluble in cold water. Its boiling-point is, when pure, 220° at 40 mm. pressure. The body is insoluble in alkalies, but dissolves readily in hydrochloric acid to form the hydrochloride described above. This hydrochloride is a white, crystalline solid which partly decomposes into the free base and hydrochloric acid when it is dissolved in water.

One gram of the substance $C_{12}H_{14}N_2O$ was dissolved in an excess of alcoholic potash, and boiled for three hours in a flask fitted with an inverted condenser. After evaporating the excess of alcohol and diluting with water, the whole was extracted with pure ether, dried over calcium chloride, and the ether evaporated. There remained 0.95 gram of an oil which solidified in a freezing mixture and proved to be the unchanged base. In order to see if concentrated sulphuric acid would have any effect, one gram was dissolved in an excess of that substance and, after allowing to stand over night, was warmed for some time at 50°, cold water was then added, the mixture rendered alkaline with a solution of sodium hydroxide, and extracted with ether. After drying over calcium chloride and evaporating the ether, 0.8 gram of unchanged substance remained. The loss of 0.2 gram may be due to some decomposition, but as yet I have not had an opportunity to reinvestigate the subject. The body $C_{12}H_{14}N_2O$ readily forms a dibrom addition-product when treated with pure bromine in absolute chloroform solution. This dibrom addition-product is a solid which crystallises in large, colorless prisms having a melting-point of from 111° to 112°.

In order to obtain some insight into the constitution of $C_{12}H_{14}N_2O$, the substance was heated with an excess of methyl iodide in a sealed tube for some hours at 100°. On opening the tube, evaporating the unchanged iodide, and removing iodine by means of molecular silver, a thick syrup remained, which was dissolved in water, filtered from a small quantity of an insoluble red solid, and evaporated to dryness. This operation was repeated until the product was perfectly soluble in cold water, when the whole was placed in a vacuum desiccator and put aside to crystallise. After standing for some weeks the substance had become only partially solid, so an attempt was made to fraction it *in vacuo*, but it was found that during this operation complete decomposition set in, with the formation of a basic oil which had the odor of pyridine. The formation of a soluble product by the action of methyl iodide on the body $C_{12}H_{14}N_2O$ reminds us very forcibly of the similar reaction of 1-phenyl-3-methyl-5-pyrazolon, and leaves no doubt in my mind that the two nitrogen atoms in the substance under consideration are present in exactly the same atomic relations as they are in that substance.

The alkaline extract of the original ethereal solution obtained from the action of phenylhydrazine hydrochloride on acetoacetic ether was exactly neutralised with hydrochloric acid, when a solid substance separated. The latter was repeatedly recrystallised from hot water, from which it separates in crystalline aggregates of concentric needles having a melting-point of 127°, and which from analysis proved to be 1-phenyl-3-methyl-5-pyrazolon. The identity of the latter was further confirmed by conversion into pyrazol-blue. Phenylmethylpyrazolon is the chief product of the reaction between phenylhydrazine hydrochloride and acetoacetic ether.

The Action of Acetyl Chloride on the Phenyl Hydrazide of Acetoacetic Ether.

The phenyl hydrazide of acetoacetic ether was prepared according to Nef's[1] method, and then an ethereal solution of the latter mixed with an excess of acetyl chloride and allowed to stand. Hydrochloric acid was evolved, and an oily layer separated at the bottom of the flask. The whole was then poured into ice-water and repeatedly extracted with alkalies, dried over calcium chloride and evaporated. A yellow oil remained, which, after fractioning *in vacuo*, was cooled in a freezing mixture. After the oil had solidified it was spread on a porous plate, and finally purified by dissolving in absolute alcohol and precipitating with ice-water. When so purified it melts at 36°, and has all of the properties of the solid melting at 36° obtained by the action of phenylhydrazine hydrochloride on acetoacetic ether. The alkaline extract of the ethereal solution was exactly neutralised with hydrochloric acid, when a solid separated, which, after recrystallisation, proved itself to be phenylmethylpyrazolon. The products of the action of acetyl chloride on the phenylhydrazide of acetoacetic ether are therefore identical with those obtained by the action of phenylhydrazine hydrochloride on the latter substance.

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[1] Ann. Chem. (Liebig) **266**, 170.

The Action of Hydrobromic Acid on Acetoacetic Ether.

Thirty-seven grams of acetoacetic ether were mixed with three volumes of perfectly dry ether cooled to —15°, and dry hydrobromic acid gas was passed in until the mixture was perfectly saturated. The whole was then allowed to stand over night, the ether was evaporated by passing a current of dry air through the contents of the flask. There remained a dark-brown oil which was fractioned; 9 grams passed over between 85° and 100°, 19.3 grams between 100° and 125°, 12.6 grams between 281° and 300°, and 6.6 grams between 330° and 360°. The lower fraction consisted of a mixture of ethyl bromide and alcohol and acetic ether. The fraction between 100° and 125° separated into two layers, the upper one of which contained acetone, alcohol and aqueous hydrobromic acid, the lower was ethyl bromide and acetic ether mixed with a high-boiling fraction. The fraction from 281° to 300° was carbacetacetic ether, while the one from 330° to 360° is as yet unidentified. Dry hydrobromic acid, in ethereal solution, therefore completely decomposes acetoacetic ether, its action being exactly parallel to that of hydrochloric acid.

Better results were obtained by the following means. A flask holding 12.5 liters was filled with dry hydrobromic acid gas, and after being placed in an open court during a very cold winter day, the calculated equimolecular quantity of acetoacetic ether (82.5 grams) was quickly poured in, the flask stoppered and allowed to stand for one hour at a temperature below 0°. The hydrobromic acid was almost completely absorbed, the stopper of the flask being pressed into the neck owing to the vacuum which had been created within. The product of the reaction was repeatedly shaken out with ice-water, the remaining heavy oil quickly dried over calcium chloride, and a bromine determination made.

0.1992 gram substance gave 0.0613 AgBr. Found Br = 13.09 per cent.

The results of a second determination were as follows: 0.2392 gram substance gave 0.0658 gram AgBr. Found Br = 11.7 per cent.

From these analyses it is evident that the major portion of the hydrobromic acid which was contained in the acetoacetic ether had been removed by the repeated washings with ice-water. On fractioning the oil which had been obtained, hydrobromic acid was given off and the oil separated into three portions; one, boiling from 70° to 100°, contained alcohol and ethyl bromide; the middle fraction, which was by far the largest, consisted of unchanged acetoacetic ether; while the highest-boiling one was carbacetoacetic ether. If the oil obtained after washing with ice-water is shaken with alcoholic potash, the hydrobromic acid is completely removed, and the product, with the exception of a little high-boiling substance, consists of unchanged acetoacetic ether. A similar result is obtained from the action of zinc ethyl on the dried oil containing hydrobromic acid. The hydrobromic acid addition-product of acetoacetic ether is therefore extremely unstable, and indeed, has much more of the character of a simple solution than of an additive product in which dissociation of the hydrobromic acid has taken place.

THE ATOMIC WEIGHT OF PALLADIUM.

BY HARRY F. KELLER AND EDGAR F. SMITH.

Two years ago[1] we showed that palladium can be completely precipitated by the electric current from a solution of palladodiammonium chloride in ammonia. In the same paper we expressed the belief that this behavior would afford an excellent means of determining the atomic weight of palladium, and we further stated that it was our intention to extend our investigation in this direction. Aside from the consideration that the atomic weight of every element should, if possible, be determined by more than one method, there were other reasons that led us to undertake a redetermination of this constant. The results published by different experimenters were few and discordant, and a critical examination of the methods employed by them seemed to show that the determinations were infected through various sources of error.

Berzelius was the first to determine the atomic weight of palladium. From his analysis of potassium palladous chloride, made in 1828,[2] the number 106.2 was deduced, which was generally conceded to be the most trustworthy, until Keiser in 1889,[3] by determining the amount of metal in palladammonium chloride, obtained the number 106.35.

That a high degree of accuracy cannot be claimed for Berzelius' number is evident, since he himself states that he did not succeed in completely dehydrating his salt without an appreciable loss of chlorine, and further, it is doubtful whether he succeeded in entirely eliminating the numerous impurities which occur in the commercial metal.

Keiser's value is the mean of two well-agreeing series of determinations which were apparently made with both skill and care; it is but slightly higher than that of Berzelius; both accord quite well with the position of the element in the periodic system. Nevertheless, we suspected that even these later determinations were not free from errors. Thus, we had found that Wilm's method, employed by Keiser in the preparation of his palladammonium chloride, does not give a product that is absolutely free from foreign metals, especially copper; and some observations made by us, while igniting the yellow salt, pointed to a probable loss of material during the reduction in hydrogen.

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[1] This Journal **12**, 212.

[2] Pogg. Annalen **13**, 455; Lehrbuch **3**, 1213.

[3] This Journal **11**, 398.

The value ($Pd=111.88$), calculated by Quintus Icilius[1] from his analysis of potassium pallado-chloride, differs so widely from the results of all other experimenters that it scarcely deserves serious consideration.

Preparation of Pallado-diammonium Chloride.

The crude palladium used in the preparation of the salt employed for the determination of the atomic weight was procured from the well-known firm of W. C. Heraeus in Hanau. It weighed about 28 grams and was in the form of foil. In a letter to one of us, Mr. H. Heraeus described the process by which it had been obtained, as follows:

Platinum ore is dissolved in aqua regia. After the insoluble residue has subsided, the clear supernatant liquid is drawn off and the platinum precipitated by ammonium chloride. The double salt is then separated from the mother-liquor and well washed. Filtrate and washings are united and mixed with metallic iron. The metals thereby thrown down are boiled with hydrochloric acid and dissolved in aqua regia, whereupon the precipitations by ammonium chloride and iron are repeated. After treatment with hydrochloric acid, the metals are again dissolved in aqua regia, the excess of the latter removed by evaporation and the residue taken up in dilute hydrochloric acid. Ammonia is now added to remove the iron, the solution warmed and filtered. From the filtrate the palladium is precipitated as palladammonium chloride. This salt is filtered off, washed, dried and ignited; the resulting metal being further purified by reconverting it into the yellow salt and then igniting the latter.

Mr. Heraeus also stated that the metal thus extracted is generally contaminated with copper and platinum. A qualitative examination showed that in addition to these, rhodium, gold, and iron were present in notable quantities.

To effect a removal of all these impurities the following process was, after some preliminary experiments, adopted:

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[1] Inaugural Dissertation, 1847.

The crude metal was dissolved in aqua regia, the excess of the latter removed by evaporation on the water-bath, and the residue digested with dilute hydrochloric acid. Everything passed into solution. After diluting with water, ammonia was added in excess and heat applied until the red palladammonium salt was dissolved. A reddish-brown precipitate, consisting of ferric hydroxide and a rhodium compound [$Rh_2(NH_3)_{10}Cl_6$], remained; it was removed by filtration and the filtrate treated with an excess of hydrochloric acid; yellow palladammonium chloride was precipitated, and after the lapse of 48 hours this was filtered off with the aid of an air pump, thoroughly washed and drained. It was then redissolved in cold, dilute ammonia water[1] and separated from the small amount of the yellowish rhodium compound which remained undissolved. From the filtrate the palladammonium chloride was reprecipitated.

When dry, this salt was cautiously ignited in the air,[2] and the residual bluish-green mass then reduced in a current of hydrogen. The resulting metal was dissolved in aqua regia, the excess of which was afterwards expelled on the water-bath and by repeated evaporation with hydrochloric acid. The remaining chloride was then digested with water containing sufficient hydrochloric acid to dissolve it, and the solution carefully neutralised with sodium carbonate. The calculated amount of mercuric cyanide, dissolved in water, was next added: an immediate precipitation of yellowish palladous cyanide was produced. After this had been allowed to settle for several days in a warm place, the clear supernatant liquid was syphoned off. The precipitate was washed, first by decantation, then on the filter, and thoroughly drained with the air-pump. By ignition it was reduced to the metal, the highest heat of the muffle-furnace being maintained during four hours, to ensure the complete expulsion of any mercury that might have been present.

The resulting product was extracted with hydrochloric acid, to remove oxide of copper, and again dissolved in aqua regia. After repeated evaporations with hydrochloric acid, the diluted solution of palladous chloride was saturated with sulphur dioxide, whereby it assumed a bright yellow color; a slight precipitation occurred upon standing, appearing partly as a metallic mirror upon the sides of the flask, and partly in the form of dark flakes. It was found to consist of gold—by the purple of cassius test—and a trace of palladium. The addition of potassium sulphocyanate to the yellow solution produced a turbidity. The suspended particles were allowed to settle and recognised as the copper salt by the colors they imparted to the borax bead,—a strong blue in the oxidising flame, and a brick-red when treated with tin in the reducing flame.

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[1] Wilm, Ber. **15**, 241.

[2] In the ignitions of the salt in air we made observations similar to those recently described by Wilm (Ber. **25**, p. 220); we also found that not inconsiderable quantities of palladium are volatilised; a reddish-brown coating ($PdCl_2$?) was generally formed upon the lid and near the upper edge of the porcelain crucible. This may also explain the deposition of carbon upon the outside of the crucible.

Upon warming, the solution gradually returned to its original color, while a black precipitate separated out. When all the sulphur dioxide had been expelled by protracted boiling, the solution was filtered. What remained on the filter was soluble in nitric acid, and seemed to consist of palladium only, but was nevertheless consigned to the waste residues.

The bulk of the metal was now precipitated by warming the carefully neutralised filtrate with potassium formate. A turbulent evolution of carbon dioxide was observed, while the palladium came down in the form of a black powder. The precipitation was, however, not quite complete; the filtrate appeared yellowish, and gave upon treatment with more sodium carbonate and potassium formate an additional small precipitate which was likewise rejected.

The main precipitate of palladium was thoroughly washed and dried, transferred to a porcelain crucible, which was then covered and strongly ignited in the muffle for several hours.

The metal thus obtained had a slight tarnish, but became silver white when treated with hydrochloric acid. It weighed about two-thirds as much as the material with which we had started.

The conversion of the purified metal into palladammonium chloride was effected exactly as before described. It is scarcely necessary to mention that every precaution was observed to exclude particles of dust and filter-paper and to ensure complete washing of the salt. The adhering moisture was removed by successively placing the salt into a desiccator from which the air was then exhausted, subsequently into a steam-bath, and again into the vacuum desiccator over chloride of calcium and phosphorus pentoxide, for several weeks.

Analyses.

The perfectly dry salt was preserved in well-stoppered glass tubes. From these the different portions were rapidly transferred to the accurately weighed, silver-coated platinum dishes. The latter had never been used; they were carefully cleaned, however, to remove iron, etc. Their surfaces were smooth and even throughout. The silver deposits made from potassium-silver cyanide solution were in all cases quite uniform in appearance and perfectly white. The weights of these deposits lay between .2 and .4 gram. After washing with distilled water, the dishes were carefully dried in an oil-bath at a temperature of about 150°.

A Sartorius balance[1] of great accuracy and sensibility, and a set of carefully calibrated weights, by Westphal, were used for the weighings. The method of oscillations was employed, and great care taken to conduct the weighings under uniform conditions. The final adjustment with the rider was invariably made by each of us independently of the other, and the weighing repeated in case of disagreement.

Each series of experiments was made with a different preparation of the salt.

The first series consists of but three determinations:

I. 1.2996 grams of palladammonium chloride were dissolved in 30 cc. of pure ammonia water, the solution diluted with water to about 130 cc., and electrolysed in the cold with a current liberating 1 cc. electrolytic gas per minute. By raising the level of the liquid and thus exposing a fresh zone of silver, the completion of the precipitation was ascertained. The solution was now rapidly decanted and lukewarm water poured over the deposit. After a thorough washing, the dish was allowed to dry, first by placing it over chloride of calcium in a vacuum, subsequently by heating it in an atmosphere of carbon dioxide to 140° and again to 205°.

Weight of the silvered dish + Pd = 72.5274
Weight of the silvered dish = 71.8711
.6563

From this experiment we calculate the atomic weight to be 106.928.

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[1] We are indebted for the use of this instrument to the kindness of our friend Prof. John Marshall of this institution.

II. 1.0543 grams of the salt were treated exactly as in Exp. I.

Weight of the silvered dish + Pd = 62.33215
Weight of the silvered dish = 61.79962
.53253

By calculation the atomic weight is found to be 106.918.

III. The quantity of salt used in this experiment was 1.92945 grams. It was dissolved in 55 cc. of ammonia, diluted to 175 cc. and electrolysed with a current equivalent to 1.4 cc. of oxyhydrogen gas per minute. The deposit was washed with hot and with cold water. While yet moist it was placed in a desiccator connected with an air-pump and allowed to become dry. It was then heated in an oil-bath to 210°–215°. Carbon dioxide was not used in this experiment.

Weight of silvered platinum dish + Pd = 93.03165
Weight of silvered platinum dish = 92.05710
.97455

This result would place the atomic weight at 106.915.

Second Series.

I. 1.94722 grams of the yellow salt were dissolved in 50 cc. of ammonia water, diluted to 150 cc. and exposed for 18 hours to the action of a current liberating .8 cc. of electrolytic gas per minute. During the last hour the current was increased to 1.1 cc. of electrolytic gas per minute. The deposited metal was then washed with boiling water, dried *in vacuo*, afterwards at 110° for four hours, and finally for an hour at 150°. The weights remained constant.

Weight of silvered dish + Pd = 93.00283
Weight of silvered dish = 92.01940
.98343

The atomic weight 106.894 follows from this result.

II. 1.08649 grams of the substance were treated exactly as in the preceding experiment. The precipitated palladium was dried in an air-bath at 130° until constant weight was attained.

Weight of silvered dish + Pd = 72.65828
Weight of silvered dish = 72.10958
.54870

This corresponds to Pd = 106.885.

III. 1.28423 grams of substance were dissolved and electrolysed as in the two preceding cases. The washed deposit was treated for seven hours in an air-bath, the temperature of which was gradually raised from 110° to 150°, when the weight remained constant.

Weight of silvered dish + Pd = 62.64820
Weight of silvered dish = 61.99962
.64858

The resulting value is Pd = 106.890.

IV. The palladium salt employed for this determination weighed 1.68275 grams. It was treated in the same manner as described above.

Weight of silvered dish + Pd = 62.79500
Weight of silvered dish = 61.94490
.85010

This gives Pd = 106.955.

V. 1.69113 grams of the salt treated in the same manner gave the following result:

Weight of silvered dish + Pd = 73.18505
Weight of silvered dish = 72.33074
.85431

The calculated atomic weight of Pd = 106.949.

VI. 1.80805 grams of substance under the same conditions gave metal as follows:

Weight of silvered dish + Pd = 93.23320
Weight of silvered dish = 92.32010
.91310

Whence we deduce the value Pd = 106.896.

Results.

1st series:

Weight of Pd $(NH_3Cl)_2$.	Weight of Pd.	At. Weight.
1.29960 grams	.65630 gram	106.928
1.05430	.53253	106.918
1.92945	.97455	106.915
	Mean	= 106.920

Maximum, ...	106.928
Minimum, ...	106.915
Difference, ...	.013

2d series:

Weight of Pd $(NH_3Cl)_2$.	Weight of Pd.	At. Weight.
1.94722 grams	.98343 gram	106.894
1.08649	.54870	106.885
1.28423	.64858	106.890
1.68275	.85010	106.955
1.69113	.85431	106.949
1.80805	.91310	106.896
	Mean	= 106.911

Maximum, ...	106.955
Minimum, ...	106.885
Difference, ...	.070

The results of the two series combined give the mean value Pd = 106.914.

The calculations are based on H = 1, N = 14.01, and Cl = 35.37.

To ascertain whether the expulsion of the occluded hydrogen in the above experiments was complete, the following experiments were made:

In Experiment I, Series 2, the dish containing the palladium deposit was carefully heated over the flame of a Bunsen burner on a wide sheet of asbestos; while still hot it was transferred to a desiccator connected with an air-pump; the weight remained unaltered.

A strip of platinum was electrolytically coated with palladium, which was then washed with boiling water, dried and weighed. There was no appreciable decrease of weight when it had been successively heated to 110°, 125°, and 150°.

A piece of palladium foil, carefully weighed, was suspended as negative electrode in acidulated water. It absorbed much hydrogen, but returned to its original weight when heated to 110° and cooled in a vacuum desiccator.

To exclude dust during the depositions, the dishes were kept covered with closely-fitting glass plates.

The liquids from which the palladium had been precipitated were invariably tested with hydrogen sulphide after they had been acidified. Not the slighest change of color was observed in any case.

All deposits were regular and adhered firmly to the dishes; their color resembled that of the sheet metal, and they showed a velvet-like lustre.

The mean of our results differs from that of Keiser's by .563, or more than half a unit. In both cases the determinations were based upon the conversion of palladammonium chloride into the metal, and since the results obtained by each method agree quite satisfactorily among themselves, the cause of the discrepancy must be sought either in a difference in the degree of purity of the respective preparations employed, or in some constant error inherent in one or in both of the methods. Now it has already been thrown out in the introductory remarks to this paper that Keiser's value was probably affected by both causes. Whether, and if so to what extent this was actually the case, we have tried to ascertain by the experiments hereafter described.

It is evident from the observations we made during the purification of our palladium that the foreign metals cannot be completely eliminated by merely precipitating and reprecipitating the palladammonium salt. This fact, however, cannot be directly used as an argument in favor of our results, since Keiser's metal and ours had come from different sources and therefore did not necessarily contain the same impurities.

The firm of Eimer & Amend in New York supplied us with a sample of the palladium used by Keiser, which we have analysed with the following results:

	I.	II.	III.
Pd	94.46	93.92	94.84
Pt	...	0.50	0.41
Rh	...	...	1.45
Au	...	0.19	0.22
Cu	...	0.56	0.58
Fe	...	0.24	0.31
			97.81

Silver, lead and zinc were entirely absent. Owing on the one hand to the difficulty of effecting a complete precipitation of palladium by a single reagent (except hydrogen sulphide), and on the other to the persistent co-precipitation of small amounts of the impurities, the course of analysis became exceedingly complicated, and a loss of material was unavoidable. But while we do not claim for the above figures a very high degree of accuracy, the analyses prove conclusively that both Heraeus' and Eimer & Amend's metal had essentially the same composition.[1]

Thus it was shown that the palladammonium salt prepared by Keiser could not have been perfectly pure. That this is not the only source of error affecting his determinations will be seen from the following three series of experiments.

First Series.

Palladammonium chloride of the same preparation that had served for the electrolytic determinations was reduced by heating it in a current of hydrogen. The apparatus used for this purpose was constructed exactly as described by Keiser, and his mode of operating closely adhered to; *the substance had not been powdered.*

When heat was applied a slight decrepitation occurred and dark stains of palladium appeared in the tube, both in the immediate vicinity of the boat containing the substance and some distance away from it in the anterior part.

	Wt. of Pd $(NH_3Cl)_2$.	Wt. of Pd.	At. Wt.
1)	0.62955 gram	0.31743	106.542
2)	0.77270	0.38942	106.438
3)	0.83252	0.41918	106.240
4)	0.99055	0.49895	106.328

[1] Although no quantitative analysis of Heraeus' palladium was attempted, the process of preparing our material afforded us an opportunity of judging of the relative amounts of the foreign metals, and we can safely assert that they did not materially differ from those obtained in the analysis of Eimer & Amend's sample.

Second Series.

The material here employed was prepared from the crude metal by Wilm's method, exactly as described in Keiser's paper. The two different preparations, which we will designate as A and B, were respectively obtained from Heraeus' and Eimer & Amend's palladium.

Both in this and the following series the reduction was effected in an apparatus of modified construction. In a large generator of the Norblad pattern, hydrogen was prepared from pure granulated zinc and pure dilute sulphuric acid. It was purified by treatment with the following substances in the order given: Alkaline solution of lead acetate, pumice soaked in silver nitrate, solution of silver nitrate in water, concentrated sulphuric acid, sticks of caustic potash, calcium chloride, chips of pure copper heated to cherry-redness, calcium chloride, and pieces of glass coated with phosphorus pentoxide. By means of three-way stopcocks we were enabled to replace by dry air or pure carbon dioxide the hydrogen in the reduction-tube. A Péligot tube containing concentrated strong sulphuric acid was placed at the further end of the apparatus to prevent the entrance of air and moisture.

The salt was reduced to a fine powder in an agate mortar; otherwise the process was conducted in the same manner as in Series I. No decrepitation was observed in any of the experiments, but ill-defined gray stains in the anterior part of the tube indicated the volatilisation of palladium, which was further confirmed by the deep-red color with which these stains dissolved in aqua regia. Attempts to estimate the amount of loss thus incurred proved unsuccessful.

The experiments of this series resulted as follows:

	Wt. of Substance.	Wt. of Metal.	At. Wt.
	A.		
1)	1.02175	0.51468	106 332
2)	1.10325	0.55590	106.396
3)	0.66690	0 33590	106.310
4)	0.86840	0.43733	106.280
	B.		
5)	1.41430	0.71255	106 372
6)	1.15234	0.58050	106.346

Third Series.

The experiments of this series differed only from the preceding in that the salt prepared by our method was substituted for the less pure material. The results were as follows:

	Wt. of Substance.	Wt. of Pd.	At. Wt.
1)	0.96229 gram	0.48502 gram	106.452
2)	0.97804	0.49294	106.419
3)	0.94253	0.47517	106.510
4)	0.86090	0.43405	106.574

The fact that particles of the substance were projected from the boat during the heating satisfactorily accounts for the discrepant results of the first series. By *finely powdering* the yellow salt previous to its reduction—a precaution not mentioned by Keiser—this source of error was avoided, but it was then observed that the method is infected with a constant error—a loss of palladium through volatilisation. And since the determinations of Series 3 are distinctly higher than those of Series 2, it follows that the retention of impurities in the palladammonium chloride obtained by Wilm's method has likewise introduced a small but appreciable error.

We have thus shown that three sources of error have contributed to make Keiser's determination of the atomic weight too low.

We have also endeavored to determine the atomic weight of palladium by converting the palladammonium salt into the sulphide by heating it in a current of hydrogen sulphide.[1] The following results were obtained:

	Wt. $Pd(NH_3Cl)_2$.	Wt. PdS.	At. Wt.
1)	0.71699 gram	0.47066 gram	107.07
2)	1.31688	0.86445	107.07

While we regard these results as in a measure confirming those of our electrolytic determinations, we do not attach to them equal value.

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[1] Berichte **23**, 3373.

THE ELECTROLYTIC SEPARATION OF PALLADIUM AND PLATINUM FROM IRIDIUM.

By Edgar F. Smith.

The electric current precipitates both palladium and platinum[1] from solutions of these metals in the presence of an excess of an alkaline phosphate and free phosphoric acid. Metallic iridium under similar conditions is not precipitated, and the experiments that follow show that in this way the separation of palladium and platinum from iridium may be effected without difficulty.

Palladium from Iridium.

1. To 15 cc. palladium solution (=0.1458 gram metallic palladium) were added 30 cc. of disodium hydrogen phosphate (sp. gr. 1.0358), 5 cc. free phosphoric acid (sp. gr. 1.47), and 150 cc. of water. A current liberating 1.2 cc. electrolytic gas per minute acted upon this solution during the night. The deposit of palladium was bright and metallic in appearance, as well as very adherent. It was washed with hot water. Its weight equaled 0.1466 gram. The deposit was not thrown directly upon the platinum cathode, but upon a silver-coated platinum dish. The quantity of iridium present with the palladium was 0.1200 gram.

2. To 15 cc. palladium solution (=0.1458 gram of metallic palladium) were added 10 cc. of an iridium solution (=0.1200 gram of metallic iridium), 40 cc. of disodium phosphate (sp. gr. 1.0358), 5 cc. of free phosphoric acid (sp. gr. 1.47), and 200 cc. of water. The current that acted during the night upon this solution liberated 2 cc. of electrolytic gas per minute. The deposited metal was quite adherent and was washed with hot water. It weighed 0.1449 gram.

3. A current liberating 3 cc. of electrolytic gas per minute acted for 12 hours upon the following mixture: 10 cc. palladium solution (=0.1303 gram of metallic palladium), 50 cc. disodium phosphate (sp. gr. 1.0358), 5 cc. phosphoric acid (sp. gr. = 1.47), 10 cc. iridium sodium chloride solution (=0.1200 gram of

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[1] This Journal **13**, 206.

metallic iridium), and 250 cc. of water. The precipitated palladium weighed 0.1305 gram.

4. The conditions in this experiment were exactly like those in 3. The palladium deposit weighed 0.1299 gram.

5. With conditions similar to those in 3 and 4, the precipitated palladium weighed 0.1298 gram.

6. In this experiment the quantities of the substances and the volume of the liquid were the same as in 3, 4 and 5, but the current registered 3.1 cc. electrolytic gas per minute. The precipitated palladium weighed 0.1303 gram.

The palladium was precipitated, in the preceding experiments, either upon copper-plated or silver-plated platinum dishes. The latter were found to answer better for this purpose because the precipitated palladium was washed with hot water and during the process of drying there was no danger that the silver-coating would oxidise, which may readily happen with the copper in using copper-plated vessels. When the latter are used the metal deposit should first be washed with water, and this then displaced with absolute alcohol, although the latter is apt to loosen thin films of the precipitated metal.

Platinum from Iridium.

The ease and accuracy with which palladium was separated from iridium left little question but that platinum and iridium would behave similarly. The following results prove it:

1. A current liberating 1.8 cc. of electrolytic gas per minute acted during the night upon 0.1042 gram of platinum and 0.1200 gram of iridium in the presence of 40 cc. disodium phosphate, 5 cc. phosphoric acid and 200 cc. of water. The precipitated platinum weighed 0.1048 gram. It was bright and metallic in appearance, as well as very adherent. It was washed with hot water.

2. The conditions here were precisely the same as those described in 1. The precipitated platinum weighed 0.1052 gram.

3. In this experiment the current gave 1.4 cc. electrolytic gas per minute, otherwise the conditions were the same as in 1 and 2. The platinum deposit weighed 0.1035 gram.

4. The solution electrolysed contained 200 cc. of water, 50 cc. of disodium phosphate, 3 cc. of phosphoric acid, with the same quantities of metal as before, while the current liberated 2 cc. of

electrolytic gas per minute. The precipitate of platinum weighed 0.1046 gram.

5. The conditions were like those in 4, except that the current generated 1.6 cc. of electrolytic gas per minute. The weight of the precipitated platinum equaled 0.1042 gram.

The platinum metal, in these separations, was deposited upon silver-coated platinum dishes.

Rhodium is another member of the platinum group of metals that has been completely precipitated[1] by the current from an acid phosphate solution.

Numerous trials were made to separate it in this manner from iridium, and although the results were apparently accurate enough for quantitative purposes, a careful examination of the precipitated rhodium disclosed the presence of iridium, and in some instances, when the separation seemed very satisfactory, unprecipitated rhodium was discovered in the iridium solution. For the present it seems best not to publish the results that were obtained.

In the presence of an excess of sodium formate, iridium is not precipitated by a current yielded by ten Crowfoot cells. This is also true if an alkaline sulphocyanide be added to its salt solutions. It is in this and other directions that it is hoped a method will yet be found for the separation of iridium from rhodium.

The material necessary for the study of the electrolytic behavior of the platinum metals was furnished the writer by the gentlemen constituting the Council of the Am. Assoc. for the Advan. of Science. He would here tender them his sincere thanks for their liberality, and also acknowledge his indebtedness to Mr. D. L. Wallace for his constant and valuable aid in the preparation of the pure salts for this research.

CHEMICAL LABORATORY, UNIVERSITY OF PENNSYLVANIA, *June* 27, 1892.

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[1] Jr. Analyt. and Applied Chemistry 5, 201.

ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.

By H. N. Stokes.

If a little powdered anhydrous aluminium chloride be added to some ethyl trichlorsilicate, $SiCl_3(OC_2H_5)$, which is cooled by ice, it dissolves, but no reaction is observed; on removing from the ice, bubbles of gas soon appear, and the reaction often becomes violent, attended by heating of the liquid. The gas, which burns with green-edged flame and formation of hydrochloric acid, is obviously ethyl chloride. If now the liquid be gently heated it gradually becomes thick, then solid, and finally the entire amount of aluminium chloride sublimes unchanged.

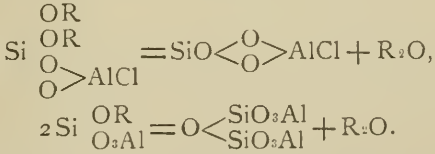
If instead of trichlorsilicate, tetraethylsilicate, $Si(OC_2H_5)_4$, be used, the reaction is in many respects the same, including the formation of ethyl chloride and the thickening of the liquid; but if the test-tube be connected with a condenser, it is seen that much ethyl ether is also produced. It may also be noticed that a relatively much greater amount of aluminium chloride than in the first case is required to produce the solid residue, while, unless a very considerable quantity has been added, none sublimes out on further heating.

It will be shown below that the action of the aluminium chloride on the trichlorsilicate is a case of so-called *catalytic action* (this being defined as a change brought about by a substance which at the end remains unaltered), while its action on the tetraethyl ether is one which is purely proportional to the relative amounts of the reagents, the aluminium remaining finally in combination with silica. It will also be seen that the monochlorsilicate, $SiCl(OC_2H_5)_3$, is intermediate in its behavior, a mere trace of aluminium chloride being sufficient to carry the decomposition to an end, when all the aluminium is found in fixed form. From these observations may be deduced the explanation of each case, including the catalytic action of the chloride on the trichlorsilicate. The details of the experiments, which were roughly quantitative, will be found in a separate section.

The only hypothesis which explains the facts observed is that in each case the substances react in a truly chemical sense, ethyl chloride and aluminium silicate compounds, Si—O—Al, being formed, but that in case of the chlorsilicates these bodies are exceedingly unstable, and decompose at once with regeneration of aluminium chloride, which is thus able to act again, and thus produce total decomposition when present even in traces.

The cause of this regeneration I take to be due, in part at least, to the tendency of the silicon to monopolise the oxygen, at the expense of the aluminium, forming Si=O, Si—O—Si, etc., whereby the metal is unable to remain combined with oxygen as long as this tendency of the silicon is not fully satisfied. If it happens that the latter is partly combined with chlorine (silicon chlorine), it at once exchanges it for an equivalent of oxygen. This, however, holds only in the aliphatic series of ethers, and in those cases where the chlorine is not the only constituent of the silicon compound. As I shall show elsewhere, silicon, when completely saturated with chlorine, as in silicon tetrachloride, does not show this tendency, neither does it exist in case of the aromatic silicates. From the latter, aluminium chloride, if in excess, takes all the oxygen and the silicon becomes completely chlorinated.

The formation of *ethyl ether* I can explain only by assuming in silicon a well-known property of carbon, which is manifested in the ortho-ethers of carbonic and other organic acids, namely, that the highest basicity is shown only when all the basic radicals are organic, while the metallic salts are of a lower degree of saturation, and the mixed organic metallic ortho-salts are so unstable as to be scarcely capable of existing under ordinary conditions. Assuming this analogy to exist, we should expect to find transformations like the following occurring:



$$\mathrm{Si}\begin{matrix}\mathrm{OR}\\ \mathrm{OR}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\!\!>\!\mathrm{AlCl} = \mathrm{SiO}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{AlCl} + \mathrm{R_2O},$$

$$2\,\mathrm{Si}\begin{matrix}\mathrm{OR}\\ \mathrm{O_3Al}\end{matrix} = \mathrm{O}\!<\!\begin{matrix}\mathrm{SiO_3Al}\\ \mathrm{SiO_3Al}\end{matrix} + \mathrm{R_2O}.$$

Strictly speaking, the tendency is not to form, as in the case of carbon, meta compounds containing Si=O, the analogue of carbonyl, but groupings in which two silicon atoms are united by oxygen, Si—O—Si, or $(\mathrm{SiO})_x$. This tendency is so strong, as has been pointed out by others,[1] that it is obviously the explanation of the fact that nearly all silicon compounds containing the analogue of carbonyl are not volatile, or volatile only at high temperatures, when by analogy with carbon, the reactions producing them should give volatile bodies of low molecular weight. This tendency to condensation and polymerisation by means of oxygen is the rule in the silicon series, and forms one of the most marked differences in the chemical behavior of these two elements, and the chief obstacle to producing by any simple means definite derivatives of silicic acid. I wish to be distinctly understood, therefore, as using the following formulas and equations only as typical ones reduced to the simplest possible form, the actual ones being vastly more complex and of almost infinite variety. Where R is used it stands, for sake of simplicity, for ethyl. That the quantitative experimental results do not conform with absolute strictness to the theoretical explanation is not surprising, for aluminium chloride is an extremely reactive body, tending to produce all sorts of secondary changes, while it is not to be expected that the transformations could be carried quantitatively to an end by heating the viscous and finally solid masses which result.

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[1] *e. g.* Mendelejeff, Grundlagen der Chemie, deutsch. Aufl. 767.

Ethyl trichlorsilicate, $SiCl_3(OR)$, is readily and completely decomposed by aluminium chloride, and the reaction is quite independent of the amount used, even a trace being sufficient. The products are ethyl chloride, free from ethyl ether, free aluminium chloride unchanged in amount, and finally a solid residue of the empirical composition $SiO.Cl_2$, but which in reality consists of a mixture of all sorts of complex silicon oxychlorides with free silica, the general result being expressed by the equation

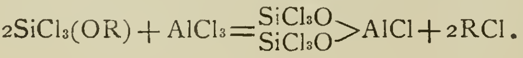
$$SiCl_3(OR) + xAlCl_3 = SiO.Cl_2 + RCl + xAlCl_3,$$

a typical case of catalytic action.

These oxychlorides are for the most part not volatile, but undergo at a high temperature transformation into oxychlorides richer and those poorer in chlorine,[1] the result being that they lose weight on ignition. The reactions by which they can be formed in the present case are very numerous, and only a few typical ones are given. The first steps in the process are

$$SiCl_3(OR) + AlCl_3 = SiCl_3.OAlCl_2 + RCl,$$

or



$$2SiCl_3(OR) + AlCl_3 = \begin{matrix}SiCl_3O\\ SiCl_3O\end{matrix}\!>AlCl + 2RCl.$$

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[1] Troost and Hautefeuille, Ann. chim. phys [5], 7, 469.

These bodies, being for reasons above given very unstable, at once react with fresh portions of trichlorsilicate,

$$SiCl_3.O.AlCl_2 + SiCl_3(OR) = SiCl_3.O.SiCl_2(OR) + AlCl_3,$$

and

$$\begin{matrix}SiCl_3O\\SiCl_3O\end{matrix}{>}AlCl + SiCl_3(OR) = \begin{matrix}SiCl_3O\\SiCl_3O\end{matrix}{>}SiCl(OR) + AlCl_3.$$

The regenerated aluminium chloride acts further, thus:

$$SiCl_3.O.SiCl_2(OR) + AlCl_3 = SiCl_3.O.SiCl_2.O.AlCl_2 + RCl,$$

which latter repeats the process, or may decompose thus:

$$SiCl_3.O.SiCl_2.OAlCl_2 = SiCl_3.O.SiO.Cl + AlCl_3,$$

and so on in every possible way *ad infinitum*, the aluminium chloride being continually regenerated, while the tendency of silicon to such condensations leads to increasing size of the molecules, which tend to the limit $(SiO.Cl_2)_x$, but seldom reach it before a high degree of complexity is attained. The increasing viscosity of the liquid interferes with the complete conversion of RO into RCl at a temperature below which other changes set in, which are manifested by more or less evolution of hydrochloric acid and gaseous hydrocarbons, with some carbonisation. There is, however, always an excess of silicon chlorine, which regenerates aluminium chloride, enabling it to act in minute amounts, and to reappear unchanged at the end.

It may be objected that these reactions are purely hypothetical, and that no such compounds as $SiCl_3.O.AlCl_2$ have been shown to exist. In the following cases it will be shown that there is strong evidence of their existence, the aluminium being caught in the act, so to speak, and found ultimately, not as chloride, but in combination with oxygen.

Ethyl monochlorsilicate, $SiCl(OR)_3$.—Aluminium chloride, in acting on this compound, produces a similar series of changes, even if used in relatively small amount, with this difference, that as there is not enough silicon chlorine to carry the regeneration through to the end, the aluminium remains finally as Al_2O_3, and probably also as AlCl, combined with silica. The process is also complicated in certain cases by the formation of ethyl ether, which was explained above.

If we suppose the aluminium chloride to act by contact or influence merely, the decomposition would be expressed by the equation

$$SiCl(OR)_3 + xAlCl_3 = SiO_2 + RCl + R_2O + xAlCl_3,$$

and the result would be practically independent of the amount of chloride used, which could be finally recovered unchanged. It is found, however, that while a mere trace is sufficient to bring about total decomposition in nearly the sense of the last equation, by increasing the amount more ethyl chloride and less ethyl ether are formed; when a certain proportion is reached, the ethyl ether vanishes, and also up to this point all aluminium remains fixed in the residue. If more than this amount of chloride be taken, some remains unchanged, and may be recovered by sublimation. We may consider three distinct cases, with differing proportions of the reagents, namely, when

$$Si : Al \begin{cases} > 3:2 & (1) \\ = 3:2 & (2) \\ < 3:2 & (3) \end{cases}$$

The first case includes that where aluminium chloride is present only in traces, when the complete reaction, reduced to the simplest form and neglecting aluminium, would be

$$(a) \qquad SiCl(OR)_3 = SiO_2 + RCl + R_2O.$$

By increasing the proportion of chloride we have, for example,

$$20SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_{20}(Al_2O_3) + 26RCl + 17R_2O,$$
$$6SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_6(Al_2O_3) + 12RCl + 3R_2O, \text{ etc.}$$

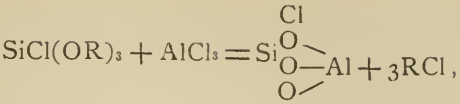
It will be noticed that the relative amount of R_2O decreases and that of RCl increases as we approach the ratio $Si : Al = 3 : 2$. Reaching this point, which is case (2), we have

$$(b) \qquad 3SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_3(Al_2O_3) + 9RCl.$$

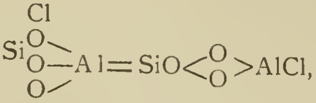
The experiment shows that with this ratio no R_2O is formed, and that all aluminium remains in fixed form in the residue. Any further increase in the proportion of chloride belongs under case (3), where $Si : Al < 3 : 2$. For example, if the ratio be that of equality, or 3 : 3, we might have

$$(c) \qquad 3SiCl(OR)_3 + 3AlCl_3 = (SiO_2)_3(Al_2O_3) + AlCl_3.$$

In fact, when this proportion is taken, unchanged aluminium chloride sublimes out of the residue. Owing, however, to the tendency of the silicon to monopolise the oxygen or to take the metasilicate form, this proportion admits of another reaction :

(*d*)


$$SiCl(OR)_3 + AlCl_3 = Si\overset{Cl}{\begin{matrix}O\diagdown\\O-\\O\diagup\end{matrix}}Al + 3RCl,$$

and


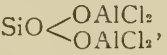
$$Si\overset{Cl}{\begin{matrix}O\diagdown\\O-\\O\diagup\end{matrix}}Al = SiO{<}^{O}_{O}{>}AlCl,$$

the residue being a chloraluminium metasilicate, or at least some similar form in which the preference of silicon for oxygen before chlorine is satisfied. The chlorine and aluminium in this form are practically fixed, as such a body as this would probably give off aluminium chloride, if at all, only at a high temperature, the effect being that the volatile chloride falls below the theoretical amount required by equation (*c*).

Finally, if Si : Al = 1 : 2—

(*e*) $$SiCl(OR)_3 + 2AlCl_3 = SiO_3Al_2Cl_4 + 3RCl.$$

If we write the formula of the product



$$SiO{<}^{OAlCl_2}_{OAlCl_2},$$

it appears that in this form also the aluminium might be fixed, but that if more chloride be present, leading to the formation of

$$SiCl(OAlCl_2)_3,$$

such a body would, by virtue of the silicon chlorine present, decompose at once into $AlCl_3$ and $SiO(OAlCl_2)_2$. Two atoms aluminium are therefore the most that can possibly be held by one atom silicon reacting as monochlorsilicate; any further amount must remain finally as unchanged chloride. The stability of such bodies as $SiO(OAlCl_2)_2$ is, however, made improbable by the experiments, which show that even with the ratio 1 : 1 only a part of the aluminium remains fixed.

These equations do not explain the semi-catalytic action of aluminium chloride in decomposing indefinitely large amounts of monochlorsilicate. The reason is obvious when we consider that, as the experiments show, the greatest amount of aluminium which can be held fixed by 1 mol. wt. monochlorsilicate, lies between $\frac{2}{3}$ and 1 at. wt. (equations *b* and *d*). Any greater amount of monochlorsilicate will, by virtue of its silicon chlorine, regenerate aluminium chloride, and be destroyed thereby, until the above proportion is reached. At this point further reaction results only in the sense of *b* and *d*, the regeneration of the chloride ceases, and all aluminium remains fixed.

It will be observed that in these reactions the chlorine going to form ethyl chloride comes proximately from the aluminium chloride, but ultimately, in part, from the chlorsilicate, and that the equations

$$SiCl_3(OR) = SiOCl_2 + RCl,$$
$$SiCl(OR)_3 = SiO_2 + RCl + R_2O$$

are not strictly true, the aluminium acting as the agent by which Cl is transferred from Si to R. The hypothesis might perhaps be further tested by substituting aluminium bromide for the chloride. If the decomposition is due to *influence* only, $SiCl_3(OR)$ should give $SiOCl_2$, and RCl and $AlBr_3$ only, but on the above hypothesis $SiO.Cl_2$ with either RBr and $AlCl_3$ only, or a mixture of RCl, RBr, $AlCl_3$ and aluminium chlorobromides, according to the proportions and the nature of the intermediate products. As this would involve previously studying the question whether a *direct* interchange of chlorine and bromine might occur, the experiment was postponed.

Ethyl dichlorsilicate, $SiCl_2(OR)_2$, from similar considerations, should decompose thus—

$$SiCl_2(OR)_2 = SiO_2 + 2RCl,$$

and it is not possible to devise any probable reaction by which aluminium should remain permanently combined. Therefore the apparent catalytic action should be as obvious here as in the case of the trichlorsilicate. The experiments were, however, defective, probably owing to impure material, and no satisfactory conclusion could be drawn from them.

Ethyl orthosilicate, $Si(OR)_4$.—This body shows a radically different behavior from that of the chlorsilicates, the decomposition being strictly proportional to the relative amount of aluminium chloride used, and in this lies the explanation of the whole series of observations.

We may consider the following cases:

$$Si : Al \begin{cases} < 3:4 & (1) \\ = 3:4 & (2) \\ > 3:4 & (3) \end{cases}$$

the ratio 3:4 being that in which the aluminium chloride contains just enough chlorine to convert all ethyl into ethyl chloride.

(*a*) $$3Si(OR)_4 + 4AlCl_3 = Si_3O_{12}Al_4 + 12RCl.$$

From considerations mentioned while speaking of the monochlorsilicate, it is obvious that this proportion may result in a certain amount of chlorine remaining combined with the aluminium, up to the limit—

(*b*) $$3Si(OR)_4 + 4AlCl_3 = Si_3O_{10}Al_4Cl_4 + 8RCl + 2R_2O.$$

For practical reasons given below, the substances could not be made to react in this proportion, the result being a formation of ethyl ether, ethyl chloride, and sublimation of some unchanged aluminium chloride. For the same reason a reaction in the sense of case (1) was practically not to be brought about.

If the reaction were in any sense catalytic, it would follow that by reducing the aluminium chloride below the proportion Si : Al = 3 : 4, the decomposition would still be complete, but the amount of ethyl ether would increase relatively, while that of ethyl chloride would decrease, the limit being, with a trace of aluminium chloride—

$$Si(OR)_4 = SiO_2 + 2R_2O.$$

The actual result was that while with Si : Al = 3 : 1 the decomposition was complete, and approximately in the sense

(*c*) $$6Si(OR)_4 + 2AlCl_3 = (SiO_2)_6(Al_2O_3) + 6RCl + 9R_2O,$$

the slightest diminution of the amount of chloride below this ratio was followed by some of the silicate remaining totally unchanged. With Si : Al = 3 : 0.9 for instance, it was possible to recover some of it, and with Si : Al = 150 : 1 the merest trace of decomposition was discernible. This proportion in the case of the monochlorsilicate resulted easily in total decomposition. The only possible explanation of this difference is that in the case of the chlorsilicates the apparent contact action is due to constant regeneration of aluminium chloride by silicon chlorine. The tetraethyl ether contains no silicon chlorine, aluminium chloride is not regenerated, and therefore acts only in proportion to the amount originally taken.

An experiment was made which shows the peculiar stability of silicon tetrachloride as compared with the chlorsilicates. It was supposed that since

$$SiCl_3(OR) + \text{trace } AlCl_3 = SiO.Cl_2 + RCl + \text{trace } AlCl_3,$$

by adding to tetraethyl silicate some silicon tetrachloride in the proportion required by the equation

$$Si(OR)_4 + 3SiCl_4 = 4SiCl_3(OR),$$

the chlorine of the tetrachloride would regenerate aluminium chloride, with the final result that solid silicon oxychloride and ethyl chloride would be formed. With even $Si:Al = 5:1$ and in sealed tubes at 100° no solid was formed. Only after heating at 170°, at which temperature the tetrachloride acts on the ether, did total decomposition occur.

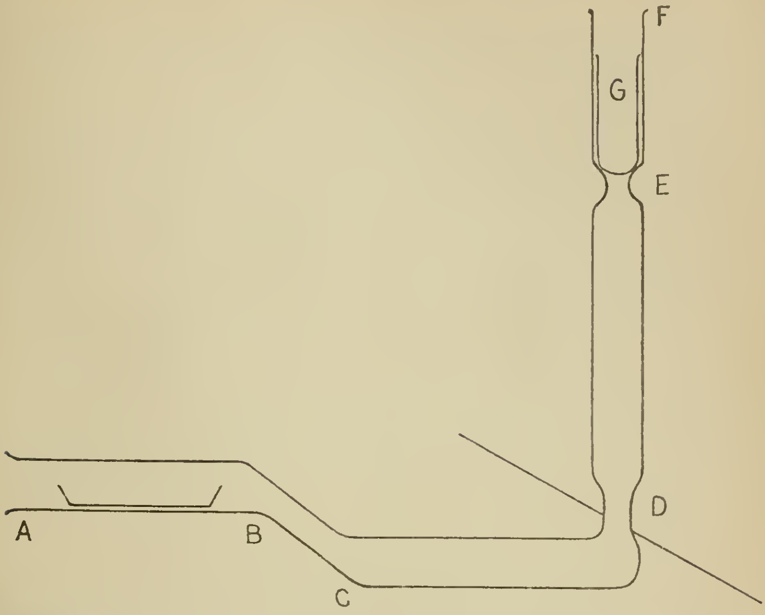
Anhydrous ferric chloride acts on both the tetraethyl silicate and the trichlorsilicate, but with much greater difficulty than aluminium chloride. Only at near the boiling-point (105°) of the trichlorsilicate was any marked reaction, with formation of ethyl chloride, visible. The tetraethyl silicate reacted easily on heating, giving off ethyl ether and ethyl chloride and leaving a solid residue. The reactions were not further studied.

Anhydrous zinc chloride is without action on the tetraethyl silicate at its boiling-point (165°).

EXPERIMENTAL DETAILS.

Only carefully fractioned silicates and freshly sublimed aluminium choride were used. The apparatus and method of working were as follows:

A thin-walled glass tube of about 2 cm. diameter was drawn out into the shape shown in the figure. The constriction *E* served when necessary as a support for the small weighed test-tube *G*, in which the ethyl ether collected. Some aluminium chloride was placed in a boat, inserted into *AB*, and carefully sublimed over into *CD* in a current of dry hydrogen. In this way it was obtained in a finely divided state, rendering solution more rapid. The hydrogen was then replaced by air, *BC* drawn out and melted off at *B*, and the weight of the sublimed chloride determined to a centigram. *CD* was then placed in ice, the calculated weight of silicate or chlorsilicate introduced through *F*, the tube *G* inserted when necessary, and the apparatus attached to an inverted con-



denser which ended in a U-tube with two cocks, placed in a freezing mixture, and serving to condense the ethyl chloride and any ethyl ether that might be carried over. By gently agitating the tube, the solution of the chloride was effected. On removing from the ice, the reaction usually began of itself, and often had to be moderated by cooling. After the evolution of ethyl chloride had slackened, *CD* was gently heated, the ethyl ether then distilling and collecting in *G*. After the collection of ether had ceased, *G* was gently warmed, whereby practically all ethyl chloride was driven over, the ether condensing and running back. After removing *G*, the point *B* was broken off and the residue heated in a current of hydrogen until no further effect was observed, any aluminium chloride condensing in *DE*, or sometimes in part being carried over into the condenser. The hydrogen was then displaced, *DF* melted off at *D*, when necessary, and all products determined by weighing. Some of the liquid in the U-tube was brought into a graduated tube over mercury, and any ethyl ether determined by absorption with a drop or two of strong sulphuric acid, the residue being ethyl chloride.

Ethyl Trichlorsilicate.

Taken $SiCl_3(OR)$ 7.66 grams (3 mol. wts.) and $AlCl_3$ 1.91 grams (1 mol. wt.).

On removing the ice from *CD*, the evolution of ethyl chloride began almost at once, and the liquid grew so warm that cooling had to be resorted to to prevent the contents from boiling over. Presently a large quantity of a colorless, apparently crystalline substance separated, nearly filling the liquid. Its nature was not determined, but it was found to fuse on gently heating. After the evolution of ethyl chloride had moderated, its formation was promoted by a gentle heat. The liquid then became gradually thick, and finally almost solid. *B* was then broken off, and the residue heated in a stream of hydrogen until no further sublimation of aluminium chloride was observed. Absolutely no ethyl ether was formed. The residue was somewhat discolored, solid, transparent and frothy. As explained above, the reaction occurs in accordance with the equation

$$SiCl_3(OR) + xAlCl_3 = SiO\,Cl_2 + RCl + xAlCl_3,$$

as is borne out by the following data, which in this as in all following experiments, are given in percentage of the total material used.

	Found.	Calculated.
Residue	46.3	51.2
Sublimate, ($AlCl_3$)	20.9	19.9
Distillate, RCl	22.5	28.8

The results are naturally only approximate, but quite as near as could be expected. The viscosity of the liquid towards the end interferes with the smoothness of the reaction, and it is impossible to condense the ethyl chloride completely, or to prevent some being carried off by the current of hydrogen. If the reactions given are correct, the residue is not really $SiO.Cl_2$, but a mixture of oxychlorides in which there remains a small amount of ethyl, which will not go off at a temperature below that at which carbonisation and other secondary changes take place, and which are still greater in the cases below mentioned. Troost and Hautefeuille[1] have shown that the result of heating oxychlorides is an approximation towards SiO_2 and $SiCl_4$. This is doubtless the reason why in this case the weight of the residue is slightly too low, and that of the sublimed aluminium chloride a little too high. The former, on extracting with alcohol, left a little silica in gelatinous form, while the latter was found to contain a small amount of volatile silicon compounds. In fact, the residue, on heating in a test-tube to redness, gave off a considerable amount of volatile oxychlorides, but no aluminium chloride.

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[1] Loc. cit.

In experiment 2, the proportions taken were the same and the observations essentially similar.

	Found.	Calculated.
Residue	38.9	51.4
$AlCl_3$ (sublimed)	21.2	19.8
RCl	22.4	28.8

The residue consisted mostly of oxychlorides, soluble in alcohol, and considerable silica (insoluble in alcohol). A portion of the same residue gave—

	Found.	Calc. for $SiO.Cl_2$.
Si	27.08	24.35

The excess of silicon is due as before to a partial volatilisation of oxychlorides with a low percentage of silicon. This residue also contained a very small amount of aluminium, which was completely extracted by alcohol, and therefore present as chloride, not as silicate or oxide. No ethyl ether was formed.

In experiment 3, the residual aluminium was determined in the residue, after heating to dull redness in hydrogen. The amount found, calculated as chloride, was only 3.5 per cent. of the total chloride used. A small amount was to be expected, as it is practically impossible to expel it completely from the solid frothy residue. The conclusion that the chloride remains unchanged at the end of the reaction may therefore be accepted without hesitation.

Ethyl Dichlorsilicate.

This calls for the reaction

$$SiCl_2(OR)_2 + xAlCl_3 = SiO_2 + 2RCl + xAlCl_3.$$

Two experiments were made, one with Si : Al = 50 : 1, the second with Si : Al = 3 : 1. In both cases the decomposition was readily brought about; in the first almost as easily as in the second, but only in the second could any aluminium chloride be recovered, and then not the whole amount used. A small amount of ethyl ether was also formed in each case. As there were reasons for suspecting the sample to contain monochlorsilicate (which would explain the discrepancy), and as no more was available, the quantitative data are omitted.

Ethyl Monochlorsilicate.

Four experiments were made in which the following proportions were observed:

$$\mathrm{Si:Al} = \left\{ \begin{array}{rl} 3:3 & \quad (1) \\ 3:2 & \quad (2) \\ 3:1 & \quad (3) \\ 150:1 & \quad (4) \end{array} \right.$$

For case (1) the following equations hold, according as the chlorine of the aluminium chloride is completely given off as ethyl chloride, or as it remains in part as $\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\!>\!\mathrm{AlCl}$.

$$(a) \qquad 3\mathrm{SiCl(OR)_3} + 3\mathrm{AlCl_3} = \mathrm{Si_3Al_2O_9} + 9\mathrm{RCl} + \mathrm{AlCl_3}.$$

$$(b) \qquad 3\mathrm{SiCl(OR)_3} + 3\mathrm{AlCl_3} = 3(\mathrm{SiO_3AlCl}) + 9\mathrm{RCl}.$$

Taken, 6.21 grams $\mathrm{SiCl(OR)_3}$ and 4.19 grams $\mathrm{AlCl_3}$, or equal mol. wts.

The course of the reaction was essentially the same as with the trichlorsilicate, except that no solid was deposited. The liquid became gradually thicker, with evolution of ethyl chloride, and then quite suddenly stiff at about 75°. On heating in a current of hydrogen, a considerable volume of uncondensible hydrocarbon gas was given off, whereby some aluminium chloride was carried into the condenser and receiver. This was collected and determined. The amount of aluminium fixed in the residue was also determined. No ether collected, and none could be found by absorption over sulphuric acid.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	37·5	28.4	45·9
Al in residue	7·3	5.4	8.1
$\mathrm{AlCl_3}$ (sublimed)	3·5	13·5	...
$\mathrm{R_2O}$	...	...	...

The reaction occurs, therefore, in a form combining (*a*) and (*b*), the residue probably consisting in part of aluminium silicates, in part of chloraluminium silicates.

For case (2) where Si : Al = 3 : 2, there are also two ultimate equations possible:

(*a*) $3SiCl(OR)_3 + 2AlCl_3 = Si_3O_9Al_2 + 9RCl.$
(*b*) $3SiCl(OR)_3 + 2AlCl_3 = Si_3O_8Al_2Cl_2 + 7RCl + R_2O.$

Taken, $SiCl(OR)_3$, 12.93 grams; $AlCl_3$, 5.80 grams; or exactly 3 : 2 mol. wts. The reaction was essentially similar to that in the last experiment, and took place quite as readily as when more chloride was used. The same gradual thickening and sudden stiffening of the liquid were noticed. On finally heating to dull redness in hydrogen, gas was evolved, and a somewhat carbonaceous black vitreous residue was left, but no aluminium chloride sublimed. A small amount of ethyl ether was formed, which was determined by absorption.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	36.0	32.7	39.1
Al in residue	6.1	6.2	6.2
$AlCl_3$ (sublimed)	...	...	...
R_2O	2.5	...	8.6
RCl	3.5	67.3	52.3

Here, too, the reaction is intermediate between (*a*) and (*b*), some R_2O is formed, but all aluminium remains in the residue.

Case (3), where Si : Al = 3 : 1, also admits of two equations:

(*a*) $6SiCl(OR)_3 + 2AlCl_3 = Si_6Al_2O_{15} + 12RCl + 3R_2O.$
(*b*) $6SiCl(OR)_3 + 2AlCl_3 = Si_6Al_2O_{14}Cl_2 + 10RCl + 4R_2O.$

Taken, $SiCl(OR)_3$, 14.72 grams; $AlCl_3$, 3.30 grams, or 3 : 1 mol. wt. The same thickening, and sudden stiffening at 75° were observed. The reaction began at the same low temperature, and was nearly as rapid as with more chloride. Ethyl ether collected in the tube *G* in abundance, and was identified by its boiling at 30°–35°. The solid residue was nearly colorless, and only on high heating did discoloration ensue. No chloride sublimed. The ether was determined by weighing that collected, and absorbing the small amount found in the distillate as before.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	43.1	31.7	38.4
$AlCl_3$ (sublimed)	...	...	...
R_2O	20.0	15.2	22.0

Although the residue was somewhat too large, the amount of ether showed that the reaction was mainly in the sense of (*b*).

Case (4). In this experiment, 1 mol. wt. aluminium chloride was made to act on 150 mol. wts. monochlorsilicate, or almost a mere trace of the former (taken, 13.38 grams silicate to 0.06 gram chloride). The facts noted were the same as in the other experiments, including the sudden solidifying of the residue. The only difference was that the reaction took place rather more slowly, owing to the small amount of chloride present, and that the residue left at red heat was of purplish color, showing very little carbonisation. The ease with which the decomposition took place indicated that a much smaller amount of aluminium chloride would have been sufficient. The ethyl ether showed the correct boiling-point.

The equation for a trace of aluminium chloride is practically

$$SiCl(OR)_3 = SiO_2 + RCl + R_2O.$$

The actual results were:

	Found.	Calculated for Si : Al = 150 : 1.
Residue	30.8	30.3
R_2O	32.7	36.8
RCl	11.2	33.0

The amount of ether was 89 per cent. of the theoretical.

Tetraethyl Silicate.

Four experiments may be mentioned, into which the following proportions entered:

$$Si : Al = \begin{cases} 3:4 & (1) \\ 3:1 & (2) \\ 3:0.9 & (3) \\ 150:1 & (4) \end{cases}$$

The hypothetical equations for (1) and (2) are given under the general considerations on the decomposition of the tetraethyl silicate (*a*, *b* and *c*).

For experiment (1) were taken 5.95 grams $Si(OR)_4$, 5.09 grams $AlCl_3$, or 3 : 4 mol. wts. It was not possible to cause the chloride to dissolve completely in this amount of ether, and the result was a mixture of varying composition, from which no definite result could be expected. The general course of the reaction was the same as in other cases. Some ethyl ether was formed, but a little aluminium chloride also sublimed, indicating an excess in one part of the mass and a deficiency in another.

In experiment (2) with $Si : Al = 3 : 1$ the mixture evolved ether and ethyl chloride, and finally became solid, and on further heating gave off gases, but no aluminium chloride. Only about one-half the theoretical amount of ether was obtained, the remainder appearing as hydrocarbon gas and empyreumatic substances.

In experiment (3) with $Si : Al = 3 : 0.9$ it was noticed that some unchanged silicate distilled at the end of the operation. It appears, therefore, that the least amount of aluminium chloride required to effect total decomposition is 1 mol. wt. to 3 mol. wts. of the silicate. This is strikingly seen in the next experiment (4), which at the same time shows the radical difference in their behavior towards aluminium chloride of the silicates and chlorsilicates.

Taken, 16.37 grams $Si(OR)_4$, 0.07 $AlCl_3$, or 150 : 1 mol. wts. Even on boiling strongly for an hour at about 165°, no marked reaction was noticed. The liquid remained clear and limpid, and not over 0.1 gram ethyl ether collected. At the end of an hour the silicic ether was distilled off unchanged, leaving but a trace of solid residue. It was therefore clear that only a trace had been decomposed, corresponding to the trace of chloride used.

The decomposition of monochlorsilicates by a trace of aluminium chloride might perhaps be utilised to obtain other ethers than ethyl ether. It is known that the continuous process for obtaining ethyl ether from alcohol by means of sulphuric acid does not apply to the alcohols above propyl alcohol.[1] Isobutyl alcohol, for instance, does not give a trace of isobutyl ether. The silicates of the monatomic aliphatic alcohols, as far as has been investigated, are easily prepared, and of all the chlorsilicates, the monochlorsilicates are the most easily made. By adding to 1 mol. wt. silicon tetrachloride 3 mol. wts. of the alcohol, boiling the product or heating to 170° under pressure, and finally distilling with a trace of aluminium chloride, a product should be obtained, consisting of a mixture of ether and chloride, which could be easily separated. From ethyl monochlorsilicate 89 per cent. of the theoretical yield of ethyl ether was thus obtained.

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[1] Norton and Prescott, This Journal **6**, 241.

On the Isolation of the Intermediate Products.

Aluminium chloride is insoluble in carbon bisulphide; if, however, a mixture of about 1 vol. tetraethyl silicate and 4 vols. carbon bisulphide be boiled with some aluminium chloride, the latter liquefies and partly dissolves, while there is an evolution of permanent gas, presumably ethyl chloride. On decanting the warm liquid a considerable amount of oil separates. This oil is not volatile, and on heating gives a solid residue resembling that obtained by the direct action of the chloride on the silicic ether. The carbon bisulphide solution, if concentrated out of contact with moisture, deposits on cooling a mass of well-formed rectangular crystals, or on evaporation *in vacuo* over paraffine shavings leaves a perfectly dry crystalline mass. A portion of such a bisulphide solution was decomposed by ammonia and the ratio of Si : Al : Cl determined. It was found to be 1 : 2.1 : 3.9, or very nearly 1 : 2 : 4, a result which may, of course, have been accidental. The oil which separates is soluble in a fresh portion of hot carbon bisulphide, but it appears readily to change, for a greater amount is required than that from which it separated, and by boiling out with small quantities of bisulphide, a residue is left which is finally almost solid. These facts seem to indicate the possibility of isolating some of the intermediate products, but this has not yet been attempted.

In conclusion, I wish to express my thanks to the Director of the Geological Survey, and to Prof. F. W. Clarke, for the means and opportunity of carrying out these experiments.

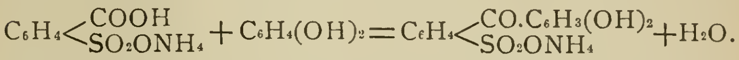
U. S. Geological Survey, Washington, *August* 1, 1892.

INVESTIGATIONS ON THE SULPHON-PHTHALEÏNS.

II.—DIOXYBENZOYL-BENZENE-SULPHONIC ACID AND SULPHON-FLUORESCEÏN.[1]

By Charles C. Blackshear.

Remsen and Linn have shown[2] that the chief product of the action of resorcin on the acid ammonium salt of ortho-sulphobenzoic acid is the ammonium salt of dioxybenzoyl-benzene-sulphonic acid, the reaction being represented thus:



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{COOH}\\ \mathrm{SO_2ONH_4}\end{matrix} + \mathrm{C_6H_4(OH)_2} = \mathrm{C_6H_4}<\begin{matrix}\mathrm{CO.C_6H_3(OH)_2}\\ \mathrm{SO_2ONH_4}\end{matrix} + \mathrm{H_2O}.$$

From the ammonium salt they prepared the free acid and from this the barium salt, and they analysed these three substances, but the acid and its derivatives were not further studied by them. At the suggestion of Professor Remsen I took up this study and the results obtained by me are recorded in this article.

Preparation of Dioxybenzoyl-benzene-sulphonic Acid.

The starting-point in the preparation of this compound was the benzoic sulphinide contained (to the extent of about 50 per cent.) in commercial saccharin. This was treated according to the method described by Remsen and Burton[3] as follows:

In a flask connected with an inverted condenser fifty grams saccharin were boiled with hydrochloric acid of such strength that thirteen parts contained one part concentrated hydrochloric acid. Within half to three-quarters of an hour all the saccharin passed into solution, and after boiling for three hours the desired transformation was complete—the solution had completely lost its sweet taste. Parasulphamine-benzoic acid crystallised from the solution on cooling. After the contents of the flask had thoroughly cooled the solution was filtered and the filtrate evaporated to dryness on the water-bath. On adding a little cold water to the residue very nearly all dissolved, and the acid ammonium salt crystallised from the filtered solution after evaporation to a very small volume. The method is very quick and effective.

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[1] From the Author's Thesis for the degree of Doctor of Philosophy, Johns Hopkins University, June, 1890.

[2] This Journal **11**, 73.

[3] This Journal **11**, 403.

The acid ammonium salt of ortho-sulphobenzoic acid being prepared, the next step is its conversion into the ammonium salt of dioxybenzoyl-benzene-sulphonic acid. This was effected by the action of resorcin in the following manner: Fifteen grams of the salt and twelve grams resorcin were placed in a small beaker which was heated gradually in a sulphuric-acid bath. A thermometer, suspended from above, was in contact with the mixture in the beaker. The resorcin melted first, and as the temperature rose the acid ammonium salt began to melt. At a temperature between 170° and 175°, and before all the acid ammonium salt had melted, the mixture was stirred with the thermometer and very soon the reaction began. The stirring was continued until the reaction became quite vigorous, and as soon as the rapidity of the reaction began to diminish it was recommenced and kept up almost continuously thereafter. After about an hour the acid ammonium salt had all melted and there was no further evolution of water. Very soon afterwards the yellow, silky crystals of the ammonium salt began to make their appearance in the dark red liquid. Crystallisation proceeded tolerably rapidly, and in the course of half an hour or so the mass was almost solid, even at this high temperature (175°–180°). The beaker was then removed from the bath and the product of the reaction was dissolved in hot water. The solution (which was reddish yellow and somewhat fluorescent) was evaporated to a small volume. On cooling, the ammonium salt separated in small yellow crystal plates arranged in aggregates. These were subsequently recrystallised after treatment with animal charcoal. With a small portion of the salt this operation was repeated several times, and finally some very nearly colorless crystals were obtained. The reaction between the acid ammonium salt of ortho-sulphobenzoic acid and resorcin takes place best at a temperature of about 180°, and the operation requires, from beginning to end, not more than two and a half to three hours. The stirring seems necessary, since in one experiment in which stirring was omitted the crystals of the ammonium salt were not formed, even though the mixture was heated at 178°–185° for nearly two days. On subsequently stirring this same mixture the reaction took place readily at 180°.

The preparation of dioxybenzoyl-benzene-sulphonic acid from its ammonium salt was effected in the following manner: To a concentrated solution in a large Erlenmeyer flask a small quantity of finely pulverised litharge was added. The solution was boiled on a sand-bath, the flask being connected with an inverted condenser. The ammonium salt is thus gradually converted into a basic lead salt, which separates as an insoluble precipitate. This basic salt was filtered off from time to time (separation from the heavier lead oxide that remained being effected by decantation), the solution evaporated to a small volume, and again boiled with lead oxide. By this method (using four large Erlenmeyer flasks and starting with a little more than fifty grams of the ammonium salt in each flask) about 210 grams of the salt were converted into basic lead salt in two to three days. During the process of boiling, crystals of ammonium carbonate appeared in the condenser tube, due evidently to slight decomposition. The solution of the ammonium salt must be concentrated, otherwise the transformation is exceedingly slow. The basic lead salt is insoluble or extremely difficultly soluble in water, but can easily be dissolved if boiled with a small quantity of water to which some acetic acid is added. The solution in acetic acid when sufficiently concentrated deposits, on cooling, crystals of moderate size. These crystals, on standing in the air, soon become opaque and pulverulent, owing, doubtless, to loss of their water of crystallisation. Analyses of these crystals gave the following results:

I. 0.26943 gram of the salt, heated two to three hours at 150°–160°, lost 0.03024 gram H_2O. Percentage H_2O, 11.22.

II. 0.25082 gram of the salt, heated two to three hours at 150°–160°, lost 0.02823 gram H_2O. Percentage H_2O, 11.26.

III. 0.29044 gram of the salt gave 0.13799 gram $PbSO_4$. Percentage Pb in crystallised salt, 32.43.

IV. 0.21651 gram of the salt gave 0.1028 gram $PbSO_4$. Percentage Pb in crystallised salt, 32.41.

V. 0.2701 gram of the salt gave 0.12892 gram $PbSO_4$. Percentage Pb in crystallised salt, 32.58.

No single formula which is plausible, and at the same time satisfies the above conditions as to percentage of lead and water, suggests itself, and the most natural inference is that the substance was a mixture of two or more basic salts of lead.

Dioxybenzoyl-benzene-sulphonic acid can be prepared from the acetic acid solution of the basic lead salt by precipitation of the lead by hydrogen sulphide. Since the acid is extremely easily soluble in both hot and cold water, it was necessary to evaporate its solution to a very small volume in order to obtain it in crystallised condition.

By adding much cold water to a very small quantity of the finely powdered, crystallised basic lead salt, solution can be effected without the addition of acetic acid, though if the solution be allowed to stand for a few minutes the basic salt will begin to separate. Now from the clear solution, from which the lead was immediately precipitated by hydrogen sulphide, colorless crystals of dioxybenzoyl-benzene-sulphonic acid were obtained. Nearly all the acid used for these investigations was prepared by the first method, that is, by precipitation of the lead from the acetic acid solution of the basic salt not previously crystallised. The crystals of the acid, as thus obtained, were always more or less dark, though by subsequent treatment with animal charcoal this color was very nearly all removed.

The acid crystallises in plates, apparently monoclinic, some of the crystals measuring as much as two to three millimeters in length and breadth.[1] When a solution of the acid is evaporated on the water-bath a yellow color is noticed on the sides of the dish near the surface of the solution, and a pink color is observable in the same parts as the solution becomes more concentrated. This is evidently due to decomposition, the acid tending, even at this temperature, to change to sulphon-fluoresceïn. The acid is soluble in alcohol, but is insoluble or only slightly soluble in ether.

Starting with 500 grams saccharin, containing about 250 grams benzoic sulphinide, the yield of dioxybenzoyl-benzene-sulphonic acid was 140 grams.

I. 0.3198 gram substance gave 0.5269 gram CO_2 and 0.1468 gram H_2O.[2] (This combustion was made by Mr. R. J. J. De Roode, Jr.)

II. 0.39665 gram substance gave 0.64221 gram CO_2 and 0.16283 gram H_2O.

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[1] The faces of the crystals were so imperfect that accurate crystallographic measurements could not be obtained.

[2] The method of combustion employed in the analyses of this acid and of sulphon-fluoresceïn was that recommended by De Roode, This Journal **12**, 226.

III. 0.38127 gram substance gave 0.61856 gram CO_2 and 0.16173 gram H_2O.

IV. 0.19193 gram substance gave 0.13045 gram $BaSO_4$ (Pearson's method).

V. 0.18916 gram substance gave 0.1263 gram $BaSO_4$ (Pearson's method).

	Calculated for $C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\ SO_2OH\end{smallmatrix} + 3H_2O$.	Found.				
		I.	II.	III.	IV.	V.
C	44.83	44.93	44.16	44.25	...	...
H	4.60	5.10	4.56	4.71	...	...
S	9.20	...	...	...	9.33	9.17

The composition of the crystallised acid as given by Remsen and Linn on the basis of sulphur estimations alone was $C_{13}H_{10}O_6S + 2H_2O$, but the above results are not reconcilable with this and indicate unmistakably a composition represented by $C_{13}H_{10}O_6S + 3H_2O$. No attempt was made to estimate the water of crystallisation, since Remsen and Linn found such an estimation impossible, on account of the tendency of the acid to change to sulphon-fluoresceïn under the influence of heat.

Barium salt, $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\ SO_3\end{smallmatrix}\right)_2Ba + 6H_2O$.—This salt (previously prepared and described by Remsen and Linn[1]) was prepared by treating a hot solution of the acid with pure barium carbonate. It crystallises in small plates which are nearly colorless. Analyses gave the following results:

I. 0.29577 gram of the salt, heated for several hours at 170°–180°, lost 0.03787 gram H_2O.

II. 0.22316 gram of the salt gave 0.06221 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\ SO_3\end{smallmatrix}\right)_2Ba + 6H_2O$.	Found.	
		I.	II.
H_2O	13.00	12.80	...
Ba	16.49	...	16.39

Calcium salt, $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\ SO_3\end{smallmatrix}\right)_2Ca + 4H_2O$.—The calcium salt was prepared by treating a hot solution of the acid with finely pulverised calcite. It is very easily soluble, even in cold water, but on evaporation to a small volume very small, thin crystals were deposited which were colorless and arranged in radial groups. The analyses resulted as follows:

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[1] Loc. cit.

I. 0.05384 gram of the salt, heated for one hour at 140°–145°, lost 0.00562 gram H_2O.

II. 0.0936 gram of the salt, heated for one hour at 140°–145°, lost 0.0099 gram H_2O.

III. 0.19723 gram of the salt gave 0.039 gram $CaSO_4$.

IV. 0.1005 gram of the salt gave 0.01977 gram $CaSO_4$.

	Calculated for $\left(C_6H_4<\substack{CO.C_6H_3(OH)_2\\SO_3}\right)_2Ca + 4H_2O$.	Found. I.	II.	III.	IV.
H_2O	10.32	10.44	10.58	...	...
Ca	5.73	...	...	5.82	5.79

Lead salt, $\left(C_6H_4<\substack{CO.C_6H_3(OH)_2\\SO_3}\right)_2Pb + 7H_2O$.—A hot solution of the acid was treated with lead carbonate in expectation of preparing a basic salt similar to the substance obtained by boiling the ammonium salt with litharge. The salt actually obtained, however, was not a basic salt but the normal salt. It is readily soluble in hot water; not very easily soluble in cold water. When its solution was evaporated on the water-bath it exhibited no tendency to change to a basic salt. The salt crystallised well, the crystals being small and apparently rhombohedral. On one occasion it was obtained in the form of long, thin crystals, but on dilution of the mother-liquor and stirring, these soon changed to the small rhombohedra. Analysis gave the following figures:

I. 0.19415 gram of the salt, heated for three hours at 145°–155°, lost 0.02642 gram H_2O.

II. 0.21537 gram of the salt, heated for three hours at 145°–155°, lost 0.02944 gram H_2O.

III. 0.19651 gram of the salt gave 0.06378 gram $PbSO_4$.

IV. 0.20673 gram of the salt gave 0.06689 gram $PbSO_4$.

V. 0.20059 gram of the salt gave 0.06492 gram $PbSO_4$.

	Calculated for $\left(C_6H_4<\substack{CO.C_6H_3(OH)_2\\SO_3}\right)_2Pb + 7H_2O$.	I.	II.	Found. III.	IV.	V.
H_2O	13.72	13.61	13.67	...	...	...
Pb	22.48	...	...	22.15	22.09	22.09

Silver salt, $C_6H_4<\substack{CO.C_6H_3(OH)_2\\SO_2OAg} + 2H_2O$.—The silver salt was prepared by treating a warm solution of the acid with pure, freshly precipitated silver carbonate. Much care was necessary in the preparation and crystallisation of the salt. The solution readily assumed a dark color. Heating seemed to facilitate this, and on evaporation of the solution on the water-bath a small quantity of a black powder separated. The salt is readily soluble in hot water and moderately soluble in cold water; it crystallises in colorless, lath-shaped crystals, radially arranged. The analyses gave the following results:

I. 0.013819 gram of the salt heated for about three hours at 100°–110°, lost 0.01162 gram H_2O.

II. 0.14157 gram of the salt, heated for about three hours at 100°–110°, lost 0.01218 gram H_2O.

III. 0.21318 gram of the salt gave 0.07556 gram Ag_2SO_4.

IV. 0.22971 gram of the salt gave 0.07395 gram AgCl.

	Calculated for	Found.			
	$C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_2OAg\end{matrix}+2H_2O.$	I.	II.	III.	IV.
H_2O	8.25	8.41	8.60	...	...
Ag	24.63	...	...	24.50	24.20

Copper salt.—This salt was prepared by treatment of a solution of the acid with freshly precipitated basic copper carbonate. Its solution was of a dark green color. Attempts at crystallisation were not attended with much success. In one instance a few extremely small crystals separated, but after standing in the mother-liquor a day or two they had apparently lost their crystalline character.

Attempted Preparation of an Ethereal Salt of Dioxybenzoylbenzene-sulphonic Acid.

In the hope of preparing an ethereal salt of the acid, both the silver and the lead salt were treated with ethyl iodide. The experiments gave negative results and may be described, briefly, as follows:

A small quantity of ethyl iodide and a few crystals of the silver salt were enclosed in a pressure bottle and the ethyl iodide was boiled for an hour or more. The crystals became opaque, but this, apparently, was the only change that took place. After filtration the filtrate was evaporated and a glutinous mass remained. This was dissolved in acetic anhydride and the solution evaporated until the odor of acetic acid had disappeared. A glutinous mass was again left. Water was added and the solution filtered from a very small quantity of solid matter. The filtrate was treated with barium carbonate. After filtration and concentration of the solution a few crystals separated. There was not enough of them for a careful examination, but tests for acetic acid showed that they were not crystals of barium acetate.

An experiment with the normal lead salt was performed in the same manner as that just mentioned, but the lead salt, in this case, was not in the least affected by ethyl iodide. Subsequently, this experiment was modified by dissolving a small quantity of the lead salt in alcohol, then adding ethyl iodide and boiling in a pressure bottle. In this case a little lead iodide separated. The solution was filtered from this, the filtrate evaporated, treated with acetic anhydride and, subsequently, with barium carbonate—exactly in the manner described in the experiment with the silver salt. The result was practically the same as with the silver salt. No crystals separated, however, after treatment with barium carbonate. On evaporation to dryness there was only a slight residue.

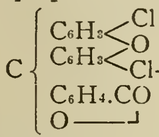
Action of Acetic Anhydride on Dioxybenzoyl-benzene-sulphonic Acid.

Several attempts were made to prepare an acetyl derivative of this acid. The experiments were conducted as follows:

Two grams dioxybenzoyl-benzene-sulphonic acid and three grams acetic anhydride being enclosed in a sealed tube, the tube was placed in a water-bath and heated to the temperature of boiling water. The acid easily dissolved in the acetic anhydride. The solution, which was of a light yellow color at first, gradually changed to red, and when, after the expiration of about three hours, the heating was discontinued it was quite red and exhibited distinct fluorescence. The solution was evaporated on the water-bath (water being added from time to time) until the odor of acetic acid could no longer be detected. It was then boiled with pure barium carbonate in order to prepare a barium salt of the substance in solution. The salt thus prepared crystallised on cooling its moderately concentrated solution, and the crystals obtained closely resembled those of the barium salt of the original dioxybenzoyl-benzene-sulphonic acid. Analyses showed that the substance actually was this salt. It is therefore clear that an acetyl derivative of this acid cannot be prepared by heating it with acetic anhydride in a sealed tube at 100°. The change in color of the solution and the fluorescence observed were probably due to the formation of a very small quantity of sulphon-fluoresceïn under the influence of heat.

Experiments with acetic anhydride at 150° and even at 170° gave no better results.

Action of Phosphorus Pentachloride on Dioxybenzoyl-benzene-sulphonic Acid.

By the action of phosphorus pentachloride on fluoresceïn Baeyer prepared a dichlor derivative of the same, represented thus:  $C\left\{\begin{array}{l} C_6H_3{<}^{Cl}_{O} \\ C_6H_3{<}^{O}_{Cl} \\ C_6H_4.CO \\ O\text{———}\rfloor \end{array}\right.$—two chlorine atoms replacing the two hydroxyl groups.[1] It seemed probable that an analogous derivative of dioxybenzoyl-benzene-sulphonic acid might be prepared—a derivative in which one or both of the hydroxyl groups of the resorcin residue would be replaced by chlorine. In the hope of obtaining such a substance, and in order to study the action of phosphorus pentachloride on the acid, whatever this action might be, the work described below was undertaken.

The first experiment was conducted in the following manner: Two grams of the acid were mixed with eight grams phosphorus pentachloride. Quite a vigorous reaction ensued. When this seemed about at an end the product was heated on a water-bath and was stirred from time to time. The liquid assumed a dark red color and became more viscous. After the expiration of about ten minutes it began to harden rapidly, and was therefore removed from the water-bath. A sample treated with dilute sodium hydroxide solution dissolved with comparative ease. This solution was decidedly fluorescent, exhibiting in transmitted light a pink color, very similar to that of eosin. Another sample was treated with alcohol, in which it dissolved with comparative ease, but no crystals could be obtained from the solution. The remainder of the product of the reaction was treated with cold water. A portion dissolved, leaving a white plastic mass; but this, too, was found to be passing into solution, and on heating dissolved with great ease. The solution was heated on the water-bath until the odor of hydrochloric acid could no longer be detected. The viscous mass remaining was diluted with water and the solution treated with barium carbonate in order to prepare a barium salt of the substance obtained. This salt crystallised well, and analysis of the same gave the following results:

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[1] Ann. Chem. (Liebig) **183**, 18.

I. 0.07937 gram of the salt, heated for an hour at 110°–120°, lost 0.01099 gram H_2O. Percentage H_2O, 13.85.

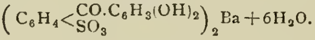
II. 0.1 gram of the salt gave 0.02858 gram $BaSO_4$. Percentage Ba in crystallised salt, 16.80.

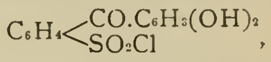
Since no definite conclusion could be deduced from these figures, another portion of the acid was treated with phosphorus pentachloride.

This second experiment was conducted in much the same manner as the foregoing. The product of the reaction between the two substances, when heated on the water-bath, was not stirred as in the former case, and, consequently, the liquid did not become hard, and the red color appeared only where the sides of the dish came in contact with the surface of the solution. The product of the reaction dissolved with comparative ease in water, even when ice was added, though not so readily. The solution was evaporated until the hydrochloric acid was eliminated, and the concentrated solution remaining was allowed to stand over night. By the next morning solid matter, arranged in spherical masses, had separated. This dissolved on addition of water. The solution was boiled with barium carbonate. On evaporation of the filtered solution a crystalline substance soon began to separate. This proved to be barium phosphate, and was filtered off after the solution had been reduced to a very small volume. From the filtrate small, flat crystals of a light yellow color separated. These contained a trace of chlorine, doubtless due to impurity. The results of the analyses show conclusively that the substance was the barium salt of the original dioxybenzoyl-benzene-sulphonic acid.

I. 0.08505 gram of the salt, heated for two and a half hours at 118°–120°, lost 0.01093 gram H_2O.

II. 0.10357 gram of the salt gave 0.02841 gram $BaSO_4$.

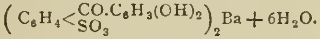
	Calculated for  $\left(C_6H_4<\substack{CO.C_6H_3(OH)_2\\ SO_3}\right)_2Ba+6H_2O.$	Found.	
		I.	II.
H_2O	13.00	12.85	...
Ba	16.49	...	16.13

It seems probable that the action of phosphorus pentachloride, or at least its chief action, led to the formation of the chloride of dioxybenzoyl-benzene-sulphonic acid,  $C_6H_4<^{CO.C_6H_3(OH)_2}_{SO_2Cl}$, and that on treating this latter with water the acid was regenerated. The investigation was continued, since it hardly seemed possible that, under proper conditions, the acid could resist further action of the phosphorus pentachloride.

The third experiment differed but slightly from the two preceding. A little more phosphorus pentachloride was used, the product of the reaction was heated on the water-bath for a longer time, until all hydrochloric acid was eliminated, and was frequently stirred meanwhile. Afterwards the red viscous mass was diluted, treated with barium carbonate and then with animal charcoal. The barium salt obtained (in connection with barium phosphate) closely resembled the barium salt of dioxybenzoyl-benzene-sulphonic acid, and contained only a trace of chlorine. The analyses given below indicate that it actually was this substance. Since the salt was, doubtless, not perfectly free from impurities, the variation from the theoretical percentages is hardly more than might be expected.

I. 0.09591 gram of the salt heated for one and a half hours at 110°–120°, lost 0.01331 gram H_2O.

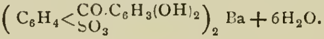
II. 0.10653 gram of the salt gave 0.02889 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4<^{CO.C_6H_3(OH)_2}_{SO_3}\right)_2Ba + 6H_2O$.	Found.	
		I.	II.
H_2O	13.00	13.88	...
Ba	16.49	...	15.95

On evaporation of the mother-liquor of the barium salt a resinous substance of a light red color separated. This became hard on cooling. A portion of it dissolved in alcohol, and on evaporation separated again, but not in crystalline form. It contained barium and also chlorine. When treated with alkali, a beautiful fluorescence was developed, and the pink color in transmitted light was strikingly like that of eosin. The substance was not of such a nature as to warrant a thorough investigation. The probability is that a portion of it consisted of the remainder of the barium salt of dioxybenzoyl-benzene-sulphonic acid, and that a very small portion, doubtless that to which the red color was due, was a chlorine derivative of sulphon-fluoresceïn, similar to eosin (tetrabrom-fluoresceïn).

The object of the experiment now to be described is the study of the action of phosphorus pentachloride on the acid at a temperature considerably higher than that of the former experiments. Two grams of the acid and somewhat more than eight grams of phosphorus pentachloride were placed in a small retort which was heated in a sulphuric-acid bath. The temperature of the bath rose gradually, and between 135° and 170° phosphorus oxychloride, together with some pentachloride, passed into the receiver. When the temperature of 170° was reached the distillation seemed about at an end, so the heating was discontinued. The product in the retort—somewhat dark in color and hard when cold—was treated with cold water. It did not dissolve to an appreciable extent. On warming it became softer, and on boiling it passed very gradually into solution. After evaporation on the water-bath to remove the hydrochloric acid present, water was added, and the solution was boiled with barium carbonate and subsequently with animal charcoal. The salt obtained (in connection with barium phosphate) separated in light yellow crystals which contained only a trace of chlorine. The analysis indicates that they were crystals of the barium salt of dioxybenzoyl-benzene-sulphonic acid, slightly impure.

0.11545 gram of the salt, heated for three hours at 120°–126°, lost 0.01619 gram H_2O and gave 0.03126 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\SO_3\end{smallmatrix}\right)_2Ba + 6H_2O.$	Found.
H_2O	13.00	14 02
Ba	16.49	15.92

A portion of this barium salt was carefully treated with sulphuric acid to remove the barium. On evaporation of the filtered solution a substance remained which possessed the characteristic properties of dioxybenzoyl-benzene-sulphonic acid. On evaporation of the mother-liquor of the barium salt resinous matter separated just as in the last experiment. In this case, however, it was not red, and when treated with alkali no fluorescence was observed. It was not investigated further.

As a result of all the above experiments it may be stated that dioxybenzoyl-benzene-sulphonic acid when subjected to the action of phosphorous pentachloride, and heated even as high as 170°, is not by any means entirely transformed into a compound in which either one or both hydroxyl groups of the resorcin residue are replaced by chlorine. If such a product is formed at all it is only to a limited extent, the chief action leading evidently to the formation of the chloride of the acid, from which the free acid is regenerated on treatment with water.

Action of Concentrated Nitric Acid on Dioxybenzoyl-benzene-sulphonic Acid.

A small quantity of dioxybenzoyl-benzene-sulphonic acid was gradually added to hot concentrated nitric acid. Reaction took place at once, accompanied by the evolution of red fumes. On subsequently boiling the acid the process of oxidation continued. After boiling for about ten minutes the red liquid was allowed to cool, when long, delicate crystals were deposited. When the nitric acid was evaporated from the mother-liquor and water added to the residue, a white substance remained undissolved, which proved to be some of the same compound, a portion of which had crystallised from the nitric acid. The melting-point of the crystals deposited by the acid solution was 174° (uncorr.), and a solution of the same in water was of a deep yellow color. These facts led to the belief that the compound was styphnic acid (trinitro-resorcin),[1] and the subsequent preparation and examination of the barium salt confirmed this. This salt was not easily soluble in hot water and very difficultly soluble in cold water. When rapidly heated on platinum foil it first assumed a red color and then exploded violently. It crystallised at first in small, orange-yellow needles. On recrystallisation very small, short, prismatic crystals were first deposited; afterwards, longer tabular crystals. Analysis of the prismatic crystals resulted as follows:

0.082 gram of the salt, heated for one hour at 192°–210°, lost 0.0039 gram H_2O and gave 0.04762 gram $BaSO_4$.

	Calculated for $C_6H(NO_2)_3O_2Ba + H_2O$.	Found.
H_2O	4.52	4.76
Ba	34.42	34.15

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[1] Stenhouse found the melting-point of styphnic acid to be 175.5°. Chem. News 23, 194.

Analysis of the needles obtained on first crystallisation gave 9.14 per cent. H_2O and 32.33 per cent. Ba. In view of the fact that barium styphnate crystallises differently under different conditions—Salkowski,[1] and Lippmann and Fleissner[2] having obtained $C_6H(NO_2)_3O_2Ba + H_2O$, and Stenhouse,[3] and Griess[4] $C_6H(NO_2)_3O_2Ba + 3H_2O$, while Henriques[5] obtained both—the figures last quoted indicate a mixture of $C_6H(NO_2)_3O_2Ba + H_2O$ and $C_6H(NO_2)_3O_2Ba + 3H_2O$.

After separating the styphnic acid as carefully as possible from the total product obtained in the reaction, the residual water solution was evaporated to a very small volume. On allowing the glutinous residue to stand for several hours it became solid and crystalline, and closely resembled ortho-sulphobenzoic acid. Two salts were prepared, the neutral barium salt and the acid barium salt. Both were colored light yellow from the presence of traces of the styphnate. The neutral salt separated in small crystals from a moderately concentrated solution. Analyses of the same resulted as follows:

I. 0.11321 gram of the salt, heated for one and a half hours at 110°–120°, lost 0.00986 gram H_2O.

II. 0.1037 gram of the salt gave 0.06457 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CO_2}_{SO_3}>Ba + 2H_2O$.	Found.	
		I.	II.
H_2O	9.65	8.71	...
Ba	36.73	...	36.61

The acid barium salt was prepared by dividing a portion of the acid into two equal parts, neutralising one part with barium carbonate and then adding the other. It crystallised in long thin needles, analyses of which gave the figures stated below. Remsen and Fahlberg[6] found that the acid barium salt of ortho-sulphobenzoic acid contained two and a half molecules of water of crystallisation, and Remsen and Dohme[7] found four and a half molecules, but the results obtained show that in this case it crystallised with two molecules.

I. 0.10467 gram of the salt, heated for one hour at 110°–120°, lost 0.00612 gram H_2O and gave 0.0426 gram $BaSO_4$.

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[1] Ber. d. chem. Ges. **8**, 637.

[2] Monatsh. Chem. **6**, 817.

[3] Chem. News **23**, 195.

[4] Ber. d. chem. Ges. **7**, 1224.

[5] Ann. Chem. (Liebig) **215**, 340.

[6] Loc. cit.

[7] This Journal **11**, 336.

II. 0.10136 gram of the salt, heated for one hour at 110°–120°, lost 0.00626 gram H_2O and gave 0.04103 gram $BaSO_4$[1].

	Calculated for $\left(C_6H_4<{COOH \atop SO_3}\right)_2Ba + 2H_2O$.	Found. I.	Found. II.
H_2O	6.26	5.85	6.18
Ba	23.83	23.93	23.80

The results above stated show conclusively that the action of concentrated nitric acid on dioxybenzoyl-benzene-sulphonic acid leads to the formation of styphnic acid and ortho-sulphobenzoic acid.

Action of Concentrated Sulphuric Acid on Dioxybenzoyl-benzene-sulphonic Acid.

The study of the action of concentrated sulphuric acid on dioxybenzoyl-benzene-sulphonic acid led to interesting results, though the time at my disposal was so short as not to permit a satisfactory examination of all the products of decomposition.

A small quantity of dioxybenzoyl-benzene-sulphonic acid was heated with a large excess of concentrated sulphuric acid in a beaker suspended in a sulphuric-acid bath. The acid soon dissolved, and the yellow color of the solution changed to a dark red as the temperature rose. At about 195°, and after stirring the liquid with the thermometer for a short time, reaction took place accompanied by the separation of dark-colored solid matter. The temperature was soon allowed to fall to 185°, and was kept at 185°–190° during the balance of the operation. The contents of the beaker were stirred at intervals. The reaction seemed to continue, though it was much less vigorous than at first. The amount of solid matter increased, but not to such an extent as to render the mass very stiff. After about two and a half hours the source of heat was removed. When the contents of the beaker had cooled, water was added to the same, and the solution was filtered. The filtrate was first examined. It was strongly fluorescent. An excess of barium carbonate was added, and the solution was subsequently filtered, treated with animal charcoal, and evaporated to a small volume. From this moderately concentrated solution a salt separated, which crystallised in prisms elongated in one direction. After a second treatment with animal charcoal and recrystallisation, the salt was obtained in colorless crystals. The properties of this salt and estimation of barium and water leave no room for doubt that it was the barium salt of ortho-sulphobenzoic acid. The analysis resulted as follows:

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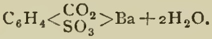
[1] Recrystallised salt was used in this second analysis.

0.11196 gram of the salt, heated for one hour at 180°–190°, lost 0.01039 gram H_2O and gave 0.07009 gram $BaSO_4$.

	Calculated for  $C_6H_4<\substack{CO_2\\SO_3}>Ba+2H_2O$.	Found.
H_2O	9.65	9.28
Ba	36.73	36.81

The dark-colored solid matter remaining on the filter was afterwards examined. On treatment with moderately concentrated caustic potash a portion of this dissolved, giving an intensely fluorescent solution. This was heated for a short time, but a considerable portion of the solid matter still remained undissolved. After filtration, hydrochloric acid was added to the fluorescent solution, when a reddish brown substance was precipitated. This substance closely resembles sulphon-fluoresceïn (described by Remsen and Linn,[1] and also in this article), the formation of which under the conditions of this experiment might have been expected; yet the percentages of sulphur and water in sulphon-fluoresceïn—sulphur 8.29 per cent., water 4.66 per cent.—are lower than the figures obtained on analysis of the substance, and no definite conclusion can be drawn without further data. The analyses gave the following results:

I. 0.04112 gram substance, heated for one hour at 125°–132°, lost 0.00215 gram $H_2O = 5.23$ per cent. H_2O.

II. 0.14637 gram substance gave 0.09607 gram $BaSO_4$ (Liebig's method) $= 9.01$ per cent. S.

The third product obtained in this reaction, which was insoluble in caustic potash, was a dark brown powder, almost black. Since it seemed insoluble in alcohol and concentrated hydrochloric acid, it was treated with these reagents, in succession, for the purpose of removing impurities. After the treatment with concentrated hydrochloric acid it was thoroughly washed with water and then dried. Estimations of the sulphur gave the following figures:

I. 0.13402 gram substance gave 0.07647 gram $BaSO_4$ (Liebig's method) $= 7.83$ per cent. S.

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[1] Loc. cit.

II. 0.12023 gram substance gave 0.06637 gram $BaSO_4$ (Liebig's method) = 7.58 per cent. S.

The substance contained water, and lost 14.08 per cent. in weight on heating for one hour at 125°–130°. On heating higher it continued to lose in weight. It seems probable that the loss at higher temperatures was due to partial decomposition, though this cannot be definitely stated. The facts established are not sufficient to warrant any speculation in regard to this compound. There is no serious difficulty involved in its preparation, and it is worthy of careful study.

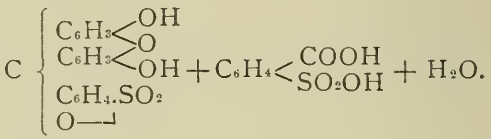
Another experiment, in which smaller quantities of dioxybenzoyl-benzene-sulphonic acid and sulphuric acid were used and a slightly lower temperature was maintained, was attended with practically the same results as the above. Analysis of the barium salt obtained gave 9.05 per cent. water, 36.65 per cent. barium. The substance similar to sulphon-fluoresceïn was considerably lighter in color than that above mentioned, but an estimation of sulphur gave 9 per cent., indicating the same composition.

Preparation of Sulphon-fluoresceïn from Dioxybenzoyl-benzene-sulphonic Acid.

Sulphon-fluoresceïn was prepared from dioxybenzoyl-benzene-sulphonic acid by heating the latter in a sulphuric-acid bath at 160°–180°, stirring quite often during the operation. The conversion takes place readily, the melted acid soon acquiring a deep red-brown color. After two to two and a half hours, when the mass had become tolerably stiff, and the reaction seemed at an end, the heating was discontinued. After becoming cool the product was treated with cold water and filtered. The sulphon-fluoresceïn remaining on the filter was thoroughly washed with cold water, and then dissolved in moderately concentrated caustic potash. On adding dilute sulphuric acid it was precipitated in yellow flocculent masses, which quickly acquired a red-brown color. The precipitate was washed a few times by decantation, and finally on the filter with the aid of a pump. The nature of the precipitate is such that washing thoroughly on the filter is a matter of great difficulty.

Sulphon-fluoresceïn is very difficultly soluble in hot alcohol and in hot glacial acetic acid. It is apparently more easily soluble in hot water than in cold, though only slightly soluble in either. In the alkalies it is easily soluble, and the fluorescence of the alkaline solution is even more intense and beautiful than that of the alkaline solution of ordinary fluoresceïn. The amount of pure sulphon-fluoresceïn obtained from 40 grams of the acid was about 16 grams. The yield was tolerably satisfactory though not quantitative, the equation representing the conversion being doubtless the following:

$2(HO)_2C_6H_3.CO.C_6H_4.SO_2OH =$



$$C\left\{\begin{array}{l} C_6H_3<^{OH} \\ \qquad O \\ C_6H_3<_{OH} \\ C_6H_4.SO_2 \\ O\text{——}\rfloor \end{array}\right. + C_6H_4<\begin{matrix}COOH\\SO_2OH\end{matrix} + H_2O.$$

Analyses of Sulphon-fluoresceïn.

Complete analyses of sulphon-fluoresceïn confirm Remsen and Linn's results as to estimation of water and sulphur, and show conclusively that the actual composition of the substance is represented by $C_{19}H_{14}O_7S$, or $C_{19}H_{12}O_6S + H_2O$.

I. 0.07929 gram substance, heated for two hours at 125°–130°, lost 0.00374 gram H_2O.

II. 0.26414 gram substance gave 0.56943 gram CO_2 and 0.10215 gram H_2O.

III. 0.2634 gram substance gave 0.56994 gram CO_2 and 0.10157 gram H_2O.

IV. 0.17089 gram substance gave 0.10099 gram $BaSO_4$ (Liebig's method).

V. 0.12418 gram substance gave 0.07046 gram $BaSO_4$ (Liebig's method).

VI. 0.12877 gram substance gave 0.07299 gram $BaSO_4$ (Liebig's method).

VII. 0.12625 gram substance gave 0.07333 gram $BaSO_4$ (Liebig's method).

VIII. 0.12788 gram substance gave 0.07544 gram $BaSO_4$ (Liebig's method).

	Calculated for	Found.							
	$C_{19}H_{12}O_6S + H_2O$.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
H_2O	4.66	4.72	...	...	...	...	...	...	...
C	59.07	...	58.79	59.01	...	...	...	...	...
H	3.63	...	4.30	4.28	...	...	...	...	...
S	8.29	...	...	...	8.11	7.79	7.78	7.97	8.10

In all the sulphur estimations except the last Keiser's modification of the Liebig method was employed.[1] The original Liebig method usually gives high results, but as modified by Keiser the results obtained are usually close and are sometimes lower than the theoretical, hence the somewhat low figures obtained are not surprising.

Contributions from the Chemical Laboratory of the U. S. Department of Agriculture.

XXI.—THE CARBOHYDRATES OF THE COFFEE BERRY.

By Ervin E. Ewell.

(*Communicated by H. W. Wiley.*)

There are few more interesting or more important fields of work for the student of plant chemistry than the one now offered in the study of the substances that go to make up the sum-total of what analysts record as "nitrogen-free extract." The recent discoveries and investigations made in this line by Dr. Schulze at Zürich, Dr. Tollens at Göttingen, Dr. W. E. Stone of Purdue, and their collaborators, have led to much investigation in this direction.

In the search for material for study, the coffee-berry has not been entirely neglected. Mr. Walter Maxwell has demonstrated[2] the presence of a galactose-yielding body in the portion of coffee insoluble in water, and succeeded in preparing a considerable amount of pure and well crystallised galactose by hydrolysis of the water-insoluble residue with dilute sulphuric acid. Reiss[3] has reported the presence of a carbohydrate that yields mannose by hydrolysis. The water-soluble carbohydrates of coffee have received less attention, and indefinite statements concerning sugar, gum and dextrin make up the existing literature of the subject.

By experiments made in the laboratory of the Department of Agriculture, cane-sugar has been shown to be the principal carbohydrate soluble in water. It is accompanied by a small percentage of a substance resembling dextrin and a small percentage of some reducing sugar. The latter may result from a slight inversion of the cane-sugar before or during the process of extraction. Pure and well crystallised preparations of cane-sugar were obtained by two different methods. The first method used, for which we are indebted to Schulze, Steiger and Maxwell,[1] may be briefly outlined as follows: The finely ground material is extracted with 70 per cent. alcohol. This extract, after treatment with lead acetate and removal of the excess of lead with hydrogen sulphide, is precipitated at the boiling temperature of the liquid with excess of strontium hydroxide. The strontium saccharate thus formed is separated by filtration, suspended in water, and decomposed by a current of carbon dioxide. After filtration from the precipitated strontium carbonate, the solution is evaporated to a sirup, which is purified by repeated solution in alcohol, evaporation and resolution, gradually increasing the strength of the alcohol. The final solution in strong alcohol is left to crystallise. In the second method, the extract is evaporated to a sirup after treatment with lead acetate, and is then directly treated with alcohol without the use of strontium hydroxide. This method is shorter and yields as good results with the material in question as does the first method described.

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[1] This Journal 5, 207.

[2] Private notes made accessible by kindness of Mr. Maxwell.

[3] Ber. d. chem. Ges. 1889, 22, 609.

For the quantitative determination of the cane-sugar, 10 grams of coffee in 1 mm. powder were extracted in a continuous percolation apparatus with absolute ether, and the residue remaining was extracted with 75 per cent. alcohol. The extraction was continued until only a very indistinct reaction for sucrose was obtained by Seliwanoff's[2] resorcinol test. The final test was made by evaporating the entire extract obtained during a day's percolation and applying the test to a small portion of this concentrated solution. After removing the alcohol by evaporation, the united extracts were treated with basic lead acetate and diluted to a definite volume. After removal of the excess of lead and inversion in the usual manner, the sucrose was estimated in an aliquot part of the solution by means of Fehling's solution, determining the cuprous oxide electrolytically. Duplicate determinations gave 6.24 and

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[1] Untersuchungen über die chemische Zusammensetzung einiger Legumenosensamen. Landwirt. Versuchs-Stationen, 1891, **39**, 269.

[2] Ber. d. chem. Ges., 1887, **20**, 181.

6.34 per cent. of sucrose. These numbers include the small amount of reducing sugar that was present.

The water-insoluble portion of coffee yields an abundance of furfuraldehyde when distilled with hydrochloric acid, sp. gr. 1.06, which indicates the presence of a pentose-yielding carbohydrate. By distillation of 5 grams of untreated coffee, 4.2–4.6 per cent. of furfuraldehyde were obtained, which is equivalent to 8–10 per cent. of a pentose (xylose or arabinose) in the original material. A gummy substance is obtained when a 5 per cent. sodium hydroxide extract is precipitated with alcohol according to the method used for the separation of xylan from wood.

When this gum is washed with alcoholic hydrochloric acid, alcohol and finally with ether, and is dried over sulphuric acid, a slightly grayish, translucent, hard and brittle mass is obtained, which is readily reduced to powder in a mortar. The properties of this substance were determined as far as the limited amount of material permitted. After hydrolysis with 5 per cent. sulphuric acid, it gave a reduction of Fehling's solution equivalent to 74.2 per cent. of dextrose; by distillation with hydrochloric acid, 13 per cent. of furfuraldehyde; by oxidation with nitric acid, 18.7 per cent. of mucic acid; and when burned, 0.84 per cent. of ash. While the small quantities of material used for these estimations precluded the desirable accuracy, the results obtained suggest a compound containing one galactose group and one pentose group. When the gum was inverted with dilute sulphuric acid, a slight flocculent residue remained. This is probably due to the slight and unavoidable turbidity of the sodium hydroxide extract and helps to account for the amount of reducing sugars obtained by hydrolysis of the gum.

Lintner and Düll[1] have reported a similar gum from barley. They found its hydrolysis product to contain equal numbers of molecules of galactose and xylose. Numbers obtained by elementary analysis agreed very closely with the theoretical percentages required by the formula $C_{11}H_{20}O_{10}$. They propose the name of "galactoxylan" for this substance. Lippmann[2] has separated a gum from sugar-beets that yields galactose and arabinose.

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[1] Über die chemische Natur des Gerstengummi, Zeitsch. f. angew. Chem., 1891, 538; Chem. Ztg. Repert., 1891, **15**, 266.

[2] Ber. d. chem. Ges. 1890, **23**, 3564; Zeitsch. f. angew. Chem. 1891, 538; Chem. Ztg. Repert. 1891, **15**, 44.

A separate portion of the water-insoluble material was hydrolysed with dilute sulphuric acid. By evaporation of the extract, after removal of the acid, a sirup was obtained that yielded an abundance of furfuraldehyde and mucic acid, showing that the pentose- and galactose-yielding substances were readily extracted by this reagent also.

The residue from the sucrose determination was heated on the steam-bath for 5 hours with 5 per cent. sulphuric acid. As the solution showed signs of darkening, it was removed from the bath at the end of this time. This strength of acid was used with the hope that the maximum amounts of pentose and galactose would be obtained, even if accompanied by a considerable amount of dextrose as a result of the partial hydrolysis of the cellulose. The extraction was incomplete, however, as the following data will show, since 4.2–4.6 per cent. of furfuraldehyde were obtained by distillation of the original material:

	Per cent. of the original material.
Reducing sugars (calculated as dextrose)	15.8
Mucic acid	5.7
Furfuraldehyde	2.6

These determinations have not been repeated under various conditions, in order to determine the proper strength of acid and length of time required for complete extraction.

Satisfactory evidence of any considerable amount of mannose in the sample of coffee used in this work has not been obtained. Parallel experiments were made with vegetable-ivory dust and coffee. With the former, an abundance of mannose-phenylhydrazon was obtained; with coffee, the slight precipitate obtained was dark-colored and insufficient in amount for a determination of its properties. The quantitative data obtained do not leave room for more than a small percentage of mannose.

Laboratory of the U. S. Dept. of Agriculture, *June* 22, 1892.

NOTES.

Carl Schorlemmer.

Carl Schorlemmer, LL. D., F. R. S., Professor of Chemistry in the Owens College, Manchester, died June 27, 1892, in his fifty-ninth year. A native of Darmstadt, his first work in chemistry was carried on in that city, and afterwards in Giessen. In 1858 he became assistant to Professor Roscoe, in the Owens College, and it is with this institution that his name has always been associated. With Roscoe he continued the work commenced by the former with the assistance of Dittmar, upon the composition of the aqueous acids. In 1861 his attention was called to the light oils produced by the distillation of cannel coal, and this led to the famous series of investigations upon the constitution of the paraffins. It will suffice to say that to a great extent we owe to him our present conception of the relations which the individual members bear to one another. Starting with the halogen derivatives of methane, he prepared its homologues successively by synthetical methods and showed them to be identical with the hydrocarbons derived from natural sources. In referring to the work by which he established the identity of dimethyl with "ethyl hydride," of "ethylpentyl" with "heptyl hydride," of "diamyl" with "decyl hydride," Sir Henry Roscoe says: "It is difficult to overestimate the importance of this apparently simple discovery. It laid forever the ghost of the existence of two sets of isomeric hydrocarbons of the paraffin series, and paved the way for Kekulé's theory of carbon combination, upon which the whole modern theory of organic chemistry is based. So to Schorlemmer belongs the credit of placing in position the foundation-stone of our science."

As an author Schorlemmer was equally distinguished. In addition to his text-books of the Chemistry of Carbon Compounds, he is everywhere known as the co-author, with Roscoe, of their great "Treatise on Chemistry," published simultaneously in England and in Germany. The section of this work devoted to the carbon compounds has been almost entirely prepared by Schorlemmer, and his death will make it necessary for another to finish the work he had brought almost to completion.

Professor Roscoe speaks of a History of Chemistry upon which Schorlemmer was engaged at the time of his death, and which he had completed down to the close of the eighteenth century. The publication of this work is promised and will be looked for with interest.

W. W. R.

Iodosobenzoic Acid.

Victor Meyer and W. Wachter give in the *Berichte*[1] an account of the preparation of what appears to be an idosobenzoic acid, $C_6H_4<\begin{smallmatrix}I=O\\CO.OH\end{smallmatrix}$, in which the atom of iodine plays the same rôle as the atom of nitrogen in the corresponding nitroso compound. Orthoiodobenzoic acid is dissolved in fuming nitric acid; a reaction evidently takes place, and, on addition of water, the new compound separates out. When the deposition takes place slowly the product is crystalline. It contains no nitrogen, but the amount of oxygen is half again as great as in iodobenzoic acid. The new compound melts at 209° with decomposition; orthoiodobenzoic acid melts without decomposition at 162°. The new acid is a strong oxidising agent; when brought together with potassium iodide, in the presence of a little sulphuric acid, iodine is set free in quantitative amount—

$$C_6H_4(IO).CO.OH + 2HI = C_6H_4I.CO.OH + H_2O + I_2.$$

On heating the acid with concentrated hydrochloric acid, chlorine is evolved. The other product in each case is orthoiodobenzoic acid. When the compound is dissolved in ammonia and treated with zinc-dust, benzoic acid is produced—a reaction characteristic of iodobenzoic acid also. The acid dissolves in the alkalies and is reprecipitated on addition of acids. If to the solution in ammonia silver nitrate be added, a precipitate of *pure iodosobenzoic acid* is produced.

No similar compound could be obtained from the corresponding chlor- and brombenzoic acids; which fact leads the authors to conclude that the third oxygen atom is held in place through some peculiarity of the iodine atom. This oxygen is not directly connected with the benzene nucleus, for under such conditions an hydroxybenzoic acid should be formed through the action of nascent hydrogen. As a matter of fact benzoic acid is the product of this action.

With aniline and with orthoamidobenzoic acid iodosobenzoic acid reacts with the formation of a product closely resembling the azo compounds; this may contain the grouping $—N=I—$, corresponding to that of the azo derivatives, $—N=N—$.

Idosobenzoic acid decolorises potassium permanganate solution. In this way an acid $C_6H_4<\begin{smallmatrix}IO_2\\CO.OH\end{smallmatrix}$ may perhaps be produced. The authors have also found that on treating benzene with a mixture of sulphuric and *iodic* acids, a crystalline product is obtained. This product had not at the time of publication of this paper been examined. The analogy with the reaction by which nitro compounds are formed leads them to suspect that the product is an iodobenzene, $C_6H_n(IO_2)_{6\ n}$. The investigation of this and similar reactions is now in progress. With respect to the corresponding meta- and paraiodobenzoic acids the authors state that no similar compound is formed by the action of nitric acid.

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[1] Ber. d. chem. Ges. **25**, 2632.

It may be noted in passing that we have not, as the Germans have, names which will distinguish between the compounds $C_6H_4.I.CO.OH$ and $C_6H_4(IO_2)CO.OH$, etc., should members of the latter class be prepared. Meyer applies the name iodobenzoic acid to the second of the two substances whose formulæ are given above.

W. W. R.

The Preparation of Hydrazoic Acid.

A new method for the preparation of hydrazoic acid, which does not involve the use of organic compounds of nitrogen, is described by W. Wislicenus,[1] and is based upon the fact that nitrous oxide reacts upon sodamide in accordance with the following equation:

$$2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3.$$

The method of procedure is as follows: Metallic sodium in small pieces is placed in a large porcelain boat and the latter inserted in a piece of combustion-tubing heated by means of a combustion-furnace. Dry ammonia is passed over the melted sodium until it has been entirely converted into sodamide. The temperature is then allowed to fall to 150°–250°, and dry nitrous oxide is substituted for the ammonia. This part of the experiment may advantageously be conducted with the tube in a Carius furnace. The mass puffs up and continues to evolve ammonia until the sodamide is completely decomposed. If a *mixture* of ammonia and nitrous oxide be passed over the melted sodium, the same reaction takes place, but the yield is not so good; in addition to this, the reaction of sodium with nitrous oxide at times produces undesirable results. The same reaction takes place in the case of potassamide, KNH_2, and of zincamide, $Zn(NH_2)_2$; in the case of zincamide the yield is poor. In each case the corresponding salt of hydrazoic acid is formed. This is dissolved in water, the solution filtered, mixed with dilute sulphuric acid, and distilled. A solution of pure hydrazoic acid collects in the receiver. The aqueous acid gives the characteristic precipitates with silver, lead and mercurous salts, dissolves gold-dust, etc.,—in short, exhibits all the properties described by Curtius.[2]

W. W. R.

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[1] Ber. d. chem. Ges. **25**, 2084.

[2] This Journal **12**, 587; **13**, 284.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. Beckurts, R. Benedikt, C. A. Bischoff, E. A. Dürre, J. M. Eder, E. Valenta, C. Häussermann, G. Krüss, M. Märcker, L. Bühring, W. Nernst, und F. Röhmann, herausgegeben von Richard Meyer. I Jahrgang. 1891. H. Bechold, Frankfurt a. M., 1892. x + 544 pp. 8vo.

The object of this publication is not to supplant the old Jahresbericht, but to present the principal results of investigations in all branches of pure and applied chemistry quickly and in readable form. There is unquestionably room for it, and many who groan under the enormous weight of current chemical literature will welcome it as a friend in need. Even the conscientious reader of the journals will find it a help, for the specialists who prepare these reports will no doubt see things that escape the ordinary reader. One cannot keep in touch with every kind of work. He who is interested in physical chemistry will, in his reading, be apt to neglect organic chemistry to some extent, and *vice versa.* Now, by the aid of the Jahrbuch der Chemie, we shall be able at the end of the year to make up our deficiencies, or at least to see where our deficiencies are. Every chemist will find the book useful. It covers a large field, including reports on (1) Physical Chemistry; (2) Inorganic Chemistry; (3) Organic Chemistry; (4) Physiological Chemistry; (5) Pharmaceutical Chemistry; (6) Chemistry of Foodstuffs; (7) Agricultural Chemistry; (8) Metallurgy; (9) Inorganic Chemical Technology; (10) Explosives; (11) Technology of the Carbohydrates and Fermentation Industries; (12) Technology of Fats; (13) Chemistry of Tar and Dyes; (14) Photography. The reports are written by chemists specially qualified for the work, and the work bears every evidence of having been done with care. Special mention should be made of the report on Physical Chemistry by W. Nernst; that on Inorganic Chemistry by G. Krüss; that on the Chemistry of Tar and Dyes by R. Meyer, and that on Photography by J. M. Eder and E. Valenta. This volume, which covers the work done in Chemistry in 1891, was published early in 1892. An equally prompt publication of the succeeding volumes is promised, the editor having adopted the motto *Bis dat qui cito dat!* I. R.

VOL. XIV. [NOVEMBER, 1892.] No. 7.

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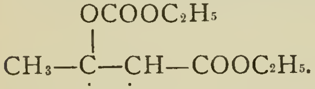
ON THE CONSTITUTION OF SODIUM ACET-ACETIC ETHER.

BY ARTHUR MICHAEL.

There are few reactions in organic chemistry that have been investigated with such different results as that of chlorcarbonic ether on sodium acet-acetic ether. Briefly mentioned by Ehrlich,[1] it was more carefully examined by Conrad and Guthzeit,[2] who supposed the product formed to be acet-malonic ether, although they found it to be a neutral oil and were unable to replace the methin-hydrogen in it by sodium. These chemists also examined the behavior of chlorcarbonic ether towards sodium malonic ether and obtained methin-tricarbonic ether, which showed a neutral character towards bases. To explain these results it was supposed that the neutral properties of these compounds are due to the grouping of three negative radicles on one carbon, an explanation which, even at that time, seemed very improbable. Lange[3] subsequently examined the action of acetyl chloride on sodium malonic ether and assumed, apparently without further examination, that the product thus formed was identical with the acet-malonic ether of Conrad and Guthzeit.

Theoretical considerations, relating to the constitutions of acet-acetic ether and its sodium derivative, induced me[4] to re-examine the work of Conrad and Guthzeit and Lange. I found the product from sodium acet-acetic ether to be, as described, a neutral oil, yielding sodium acet-acetic ether when treated with sodium ethylate; but the substance obtained by Lange from sodium malonic ether and acetyl chloride possesses entirely different properties, it having a strongly developed acid character and forming a stable sodium derivative when treated with sodium ethylate. In fact, Lange's compound represents the real acet-malonic ether, whereas the product obtained from sodium acet-acetic ether very probably has the constitution  $CH_3—\overset{OCOOC_2H_5}{\overset{|}{C}}—CH—COOC_2H_5$. It was also shown that Conrad and Guthzeit made an error in ascertaining methin-tricarbonic ether to be neutral, as it dissolves even in aqueous sodium carbonate to form a stable sodium derivative. Shortly after my paper, Claisen and Zedel[1] published a brief note stating that carb-ethoxyl-acet-acetic ether is formed from acet-acetic ether by replacing both of the methylene hydrogens by carb-ethoxyl, and therefore represents the compound $CH_3—CO—C\equiv(COOC_2H_5)_3$, a constitution which also explains its neutral character; also that methin-tricarbonic ether is in reality carbin-tetracarbonic ether, which, according to these chemists, agrees better with its properties than the constitution hitherto accepted. In view of the fact that methin-tricarbonic ether possesses strong acid properties, it might have been safely assumed at the time that Claisen and Zedel had made some experimental mistake, as this property absolutely precludes the structure which they supposed to accord better with its properties. In fact Claisen[2] corrected his statements in the same number of the *Berichte*, having found that later vapor-density determinations of carb-ethoxyl-acet-acetic and methin-tricarbonic ethers show conclusively that the compounds are mono-derivatives of acet-acetic and malonic ether.

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[1] Ber. d. chem. Ges. **7**, 892.

[2] Ann. Chem. (Liebig) **214**, 31.

[3] Ber. d. chem. Ges. **20**, 1325.

[4] This Journal **10**, 158, and more fully in J. prakt. Chem. [2] **37**, 473.

The constitution I gave to carb-ethoxyl-acet-acetic ether seems to have been pretty generally accepted, and only very recently has the subject been further investigated, when J. U. Nef,[3] in a paper on the constitution of acet-acetic ether, concluded from experimental work of his own that Claisen's first supposition is correct and therefore the substance has the structure $CH_3—CO—$

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[1] Ber. d. chem. Ges. **21**, 3397. [2] Ibid. **21**, 3567. [3] Ann. Chem. (Liebig) **266**, 52.

$C(COOC_2H_5)_3$. Nef's conclusion is based on the formation of some acet-malonic ether in the action of chlorcarbonic ether on sodium acet-acetic ether; on two combustions of carb-ethoxyl-acet-acetic ether purified by a method of his own, and "namentlich auf Grund der gemachten Erfahrungen beim Dibenzoyl- und Diacetyl-acetessigäther."[1] He rejects Claisen's and my work, owing to our having worked with an impure substance, and claims to have definitely settled the problem of the action of chlorcarbonic ether on sodium acet-acetic ether. Nothing in Nef's work appeared to the writer to justify such a conclusion. The differences between the carbon and hydrogen percentages of a mono- and di-derivative of acet-acetic ether do not amount in either case to one per cent., and in this research of Nef quite a number of analyses are stated which differ over one per cent. in carbon from the amount required by theory. Again, the amount of acet-malonic ether contained in carb-ethoxyl-acet-acetic ether, purified by repeated fractionation *in vacuo*, could not possibly have had any noticeable effect on my analyses; while the formation of diacetyl-acet-acetic ether is quite irrelevant to the subject in question, as acetyl chloride in its action on sodium malonic ether forms di- as well as mono-acetyl-malonic ether, whereas chlorcarbonic ether acting on the same compounds yields simply a mono-derivative, and, finally, the constitution I assigned to carb-ethoxyl-acetic ether accords with its properties. I had further reason to believe Nef's conclusion incorrect as I had previously examined the action of chlorcarbonic ether on sodium ethyl-acet-acetic ether, and of acetyl chloride on sodium ethyl-malonic ether, and isolated isomeric products as results of these reactions, which differed entirely in their behavior towards certain reagents. Since only one carb-ethoxyl can be introduced in ethyl-acet-acetic ether, and the compound thus formed is not only different from acet-ethyl-malonic ether, but showed by its decompositions that the introduced carb-ethoxyl is joined with oxygen, these facts evidently pointed to a similar constitution for carb-ethoxyl-acet-acetic ether. It seemed to me of importance that inaccurate observations bearing on questions so important to organic chemistry as the constitution of acet-acetic and malonic ethers, their homologues and sodium derivatives, should not be allowed to influence the judgment of chemists on the constitution of these substances, and I have therefore repeated that part of Nef's work which bears on these questions. I find my surmise of the imperfectness of this work is correct, both as regards the observation of facts and the analyses. I have also repeated my former, as yet unpublished work, with the ethyl homologues of the compounds described in my previous paper; and to confirm these results still further, the corresponding methyl derivatives were prepared and their properties examined. Before describing the experimental part of my work I wish briefly to explain my views on the constitution of acet-acetic ether, its homologues and their sodium derivatives.

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[1] Ann. Chem. (Liebig) **266**, 106.

In a former paper[1] on the constitution of sodium acet-acetic ether I called attention to the two reactions that indicate a carbinol constitution for acet-acetic ether and levulinic acid, but I further pointed out that these reactions are also explained by the assumption that these compounds contain a ketone-carbonyl, if they are considered as the final result of additions and subsequent eliminations.[2] There was therefore no valid reason for assigning to acet-acetic ether any constitution other than $CH_3—CO—CH_2—COOC_2H_5$, but in regard to its sodium derivative the formation of carb-ethoxyl-acet-acetic ether from it, as well as the results obtained by the action of carbonyl chloride and alkylene halides, are only explainable by $CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5$ representing the structure of its sodium derivative. As sodium acet-acetic ether is formed by the direct action of sodium on acet-acetic ether, it must be assumed that the product $CH_3—CO—CHNa—COOC_2H_5$ is formed at first, but, owing to the affinity of the strongly negative ketone oxygen for the very positive sodium, a molecular rearrangement immediately takes place, when the sodium passes over to oxygen with formation of the unsaturated compound $CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5$. It is, however, only the metallic derivatives of acet-acetic ether that possess this constitution, as when the metal is replaced by hydrogen a rearrangement of atoms takes place, common to all known instances where hydroxyl is joined to an unsaturated carbon in a fatty compound, and the unstable $CH_3—\dot{C}OH—\dot{C}H—COOC_2H_5$ immediately passes over into $CH_3—CO—CH_2—COOC_2H_5$. The above constitution of sodium acet-acetic ether had been previously assigned to this compound by Geuther, as a direct result of his conception of acet-acetic ether as $CH_3—COH=CH—COOC_2H_5$, but his views and mine are in all other respects essentially different. Geuther, for instance, gave ethyl-acet-acetic ether the constitution $CH_3—COC_2H_5=CH—COOC_2H_5$, although it had been proved beyond all doubt that when ethyl is introduced into acet-acetic ether it is joined to carbon and not to oxygen. To explain the formation of a carbon-homologue by the action of ethyl iodide on $CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5$, attention was called to the probability of the reaction being the outcome of an addition and subsequent elimination of sodium iodide; and not, as was generally supposed at the time, of a direct substitution. According to this interpretation the unsaturated carbons of sodium acet-acetic ether are in such a positive-negative condition as gives them a sufficiently strong affinity for ethyl and iodine to unite with ethyl iodide, the negative iodine uniting with the relatively positive unsaturated carbon and the positive ethyl with the relatively negative carbon — reactions that are expressed by the following equations:

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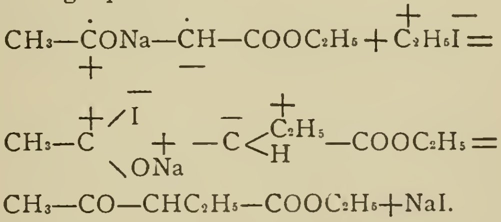
[1] J. prakt. Chem. [2] **37**, 473.

[2] Bredt (Ann. Chem. (Liebig) **256**, 314) has since endeavored to sustain the lactone constitution of levulinic acid, but I have lately published (J. prakt. Chem. [2] **44**, 113) a paper on this subject and have shown experimentally that the ketone constitution is the only one known that agrees with the properties of this acid.



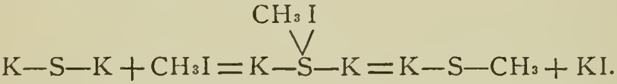
$$CH_3—\underset{+}{\dot{C}}ONa—\underset{-}{\dot{C}}H—COOC_2H_5+\overset{+}{C}_2H_5\overset{-}{I}=$$

$$CH_3—\overset{+}{C}\begin{matrix}/\overset{-}{I}\\ \backslash ONa\end{matrix}+—\overset{-}{C}<\begin{matrix}\overset{+}{C}_2H_5\\ H\end{matrix}—COOC_2H_5=$$

$$CH_3—CO—CHC_2H_5—COOC_2H_5+NaI.$$

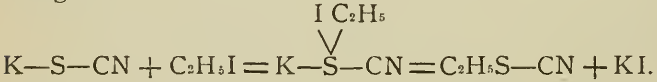
A large number of other classes of compounds which like acet-acetic ether can form sodium derivatives, as malonic and phenyl-sulphon-acetic ethers or nitro-methane, were also considered, and the general conclusion drawn that in no organic compound containing oxygen and sodium can a stable form of the compound exist in which the metal is directly joined to carbon.

The explanation given above for the formation of alkyl-acet-acetic ethers, by addition of alkyl and iodine to the unsaturated carbons and subsequent elimination of sodium iodide, led me to consider the rôle which addition plays in organic chemistry, and it was inferred that far more reactions are the results of additions than was generally supposed.[1] This subject was fully considered at the time,[2] but, as illustrations, I shall here discuss several reactions from this point of view. Methyl iodide unites readily in the cold with methyl sulphide to form trimethyl-sulphonium iodide, and this property of the sulphur of adding methyl and iodine makes it appear highly probable that methyl iodide in reacting on potassium sulphide also does it by the addition of methyl and iodine to sulphur. It can be shown that the facility with which sulphur adds methyl iodide depends on its being in a relatively positive condition, but as potassium is far more positive than methyl, the sulphur of potassium sulphide must be relatively more positive than the sulphur of methyl sulphide and should therefore unite with methyl iodide far more readily. The usual interpretation, therefore, that methyl iodide and potassium sulphide give potassium-methyl sulphide by substitution is not only a pure assumption, but is very improbable. The new conception of the reaction may be represented as follows:

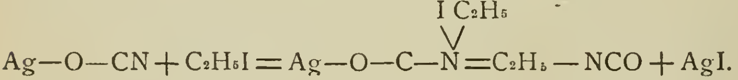


$$K—S—K + CH_3I = K—\overset{CH_3\ I}{\overset{\vee}{S}}—K = K—S—CH_3 + KI.$$

A sulphur atom, like that of methyl sulphide or of potassium sulphide, which has the power of adding alkyl halides was called relatively positive sulphur, and it probably exists in this state in KSCN. In this salt nitrogen very likely also is in a relatively positive condition, *i. e.* it may add alkyl iodides, but the sulphur, owing to its being joined directly to potassium, has a greater additive power than the nitrogen. A different condition occurs in silver cyanate, as oxygen adds under no conditions whatsoever and addition can therefore only take place on the positive nitrogen:



$$K—S—CN + C_2H_5I = K—\overset{I\ C_2H_5}{\overset{\vee}{S}}—CN = C_2H_5S—CN + KI.$$



$$Ag—O—CN + C_2H_5I = Ag—O—C—\overset{I\ C_2H_5}{\overset{\vee}{N}} = C_2H_5—NCO + AgI.$$

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[1] "Ueberhaupt scheint die besprochene Reaction gerade geeignet, um zu zeigen dass man bei Reactionen, wo die Bildung eines intermediären ungesättigten Produktes denkbar ist, nicht das Endresultat der Reaction im Licht einer vorgefassten Meinung beurtheilen darf." That this caution in my paper (J. prakt. Chem. [2] **35**, 356) on the addition of sodium acet acetic and malonic ethers to the ethers of unsaturated organic acids was timely is evident from the papers and controversies of Auwers, Bischof, Zelinsky and others that appeared several years after the above communication was published.

[2] J. prakt. Chem. [2] **37**, 507–522.

The existence of potassium sulpho-cyanate, KSCN, and of silver cyanate, AgOCN, does not imply the stability of the corresponding free acid, as hydrogen is not sufficiently positive to give permanence to such negative structures. Molecular rearrangements, therefore, take place when the metal is replaced by hydrogen, which passes over to nitrogen, and the stable forms, SCNH and OCNH, result.

A considerable number of reactions were discussed in the light of this hypothesis, and not a few hitherto unintelligible results were shown to be explainable by it. In fact the great majority of reactions were considered in which tautomerism, desmotropism or the pseudoform hypothesis had been assumed to explain the apparent existence of two structures for the same substance. In using these hypotheses, which were really rather names to imply what seemed to be facts, than explanations, a most important element had been overlooked, *i. e.* that the replacement of hydrogen by a more positive metal in those compounds that Laar supposed to have a hydrogen constantly changing its position, might cause a molecular rearrangement forming a different structure, which is stable only for the metallic derivative, as the replacement of the metal in it by hydrogen is followed by a molecular readjustment to the original constitution. This important factor, considered in connection with the phenomenon of addition, leaves, as far as I am aware, no instance where such an hypothesis is necessary, and according to this view tautomerism or desmotropism, in the sense in which that term is ordinarily used, does not exist. As this explanation of the phenomenon is materially different from previous conceptions, as is also the line of investigation it suggests, I propose to designate it by the expression *merotropy.*[1]

Action of Chlorcarbonic Ether on Sodium Acet-acetic Ether.

12.6 grams granulated sodium were brought under 600 grams pure ether, in a flask connected with an inverted cooler, and 73 grams acet-acetic ether (purified by several distillations *in vacuo*) were added in small portions and under constant shaking, so that it took about an hour before the addition of acet-acetic ether was completed. The ether was heated to boiling during the operation and finally the flask was put into a vessel of warm water and shaken for a half-hour, when the conversion into sodium acet-

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[1] See J. prakt. Chem. [2] **42**, 19; **44**, 125.

acetic ether was finished. A considerable quantity of sodium derivative had separated and the contents of the flask became thick on cooling. The flask was then well cooled off in ice-water and 59.6 grams chlorcarbonic ether gradually added from a drop-funnel, under constant shaking of the flask, which was then allowed to stand in cold water for a day. A reaction took place immediately and the greater part of the sodium derivative passed into solution, when only a small amount of the chlorcarbonic ether had been added. After standing twenty-four hours the ethereal solution still showed a slight alkaline reaction, which did not disappear on standing a longer time. The ethereal solution was shaken out several times with water and then dried over sodium sulphate.

The ether was distilled off and the residual oil, repeatedly fractionated *in vacuo*, gave unchanged acet-acetic ether and a good yield of the so-called acet-malonic ether. For analysis the latter product was fractionated several times *in vacuo*, even after a constant-boiling liquid had been obtained.

I. 0.2535 gram substance, burned with $PbCrO_4$, gave 0.4954 gram CO_2 and 0.1629 gram H_2O.

II. 0.2162 gram substance, burned with $PbCrO_4$, gave 0.4228 gram CO_2 and 0.1383 gram H_2O.

	Theory for $C_9H_{14}O_5$.	Found.	
		I.	II.
C	53.46	53.29	53.33
H	6.93	7.14	7.21

Boiling between these two ethers I obtained some oil, which I had intended to examine, but a long interruption of my work prevented me from studying this part of the reaction more carefully. Nef, making use of the observations described in my paper, succeeded in isolating some acet-malonic ether in this reaction, undoubtedly the principal part of the intermediate-boiling oil, and rejects the work done by Claisen and myself, as he thinks we worked with an impure product. I have since repeated the preparation of carb-ethoxyl-acet-acetic ether in the manner just described, and obtained by fractionation *in vacuo* a colorless oil, which boils without decomposition at 136° (20 mm. pressure, metal bath at 165°), and, even after several further re-fractionations, still gave a reddish coloration on addition of ferric chloride to its alcoholic solution, although the color was but slight. Carb-ethoxyl-acet-acetic ether cannot, according to these results, be perfectly freed from acet-malonic ether by fractionating, but the proportion of that compound contained in a product purified in this way is so small that it is not much more than a trace, as I convinced myself by extracting the acet-malonic ether from it with aqueous sodium carbonate. The portions in the above preparation boiling over 100° *in vacuo*, and the almost pure carb-ethoxyl-acet-acetic ether were separately extracted, in ethereal solution, four times with aqueous sodium carbonate, then twice with dilute aqueous sodium hydrate, and the ether solution dried over sodium sulphate. On fractionation of these products *in vacuo* a carb-ethoxyl-acet-acetic ether was obtained which gave no coloration with ferric chloride, but the boiling-point remained unchanged, it being 136° under 20 mm. and 133° under 17 mm. The analyses of this oil gave the following results:

I. 0.2332 gram oil, burnt in open tube, gave 0.4507 gram CO_2 and 0.1435 gram H_2O.

II. 0.2732 gram oil, burnt in open tube, gave 0.5335 gram CO_2 and 0.1763 gram H_2O.[1]

III. 0.2386 gram oil, burnt with $PbCrO_4$, gave 0.4689 gram CO_2 and 0.1524 gram H_2O.

IV. 0.2050 gram oil, burnt with $PbCrO_4$, gave ——— gram CO_2 and 0.1350 gram H_2O.[2]

	Theory for Acet-carbin-tricarbonic ether.	Carb-ethoxyl-acet-acetic ether.	Found.			
			I.	II.	III.	IV.
C	52.55	53.46	52.68	53.25	53.55	...
H	6.57	6.93	6.83	7.17	7.10	7.10

The small difference in the carbon and hydrogen percentages of acet-carbin-tricarbonic and carb-ethoxyl-acet-acetic ethers induced Claisen to determine the vapor-density of the compound *in vacuo*, according to Hofmann's method, as the molecular weights of the above compounds differ widely, viz. 274 and 202. Claisen states that his results leave no doubt that the compound cannot be a tricarbonic ether, but Nef[3] considers Claisen's results as inconclusive, owing to the assumed presence of acet-malonic ether in the product used by Claisen. It has already been shown that, under any circumstances, the amount of acet-malonic ether contained in a product obtained by fractionation *in vacuo* would have been too small to have had a noticeable influence on the results obtained by Claisen. However, Nef might easily have convinced himself that, even supposing the product which Claisen used for his density determinations to have contained the impossible proportion of 20 per cent. acet-malonic ether, it would not have been possible for that chemist to have gotten the results he states. To remove any uncertainty as to the molecular weight of carb-ethoxyl-acet-acetic ether I determined the vapor density of a product free from acet-malonic ether, according to Hofmann's method, using a tube about 1¼ metres long and aniline vapor, with the following results:

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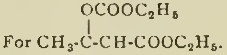
[1] Analyses I and II are given to show the great difficulty of obtaining accurate results by burning this substance in oxygen in an open tube. Analysis II was burnt in a platinum boat and the combustion-tube heated to an unusually high temperature, but even then the carbon is a little too low.

[2] The carbon was lost through an accident.

[3] Ann. Chem. (Liebig) **266**, 108.

$p = 0.024$ gram, $v = 58.3$ cc., $h_1 = 331$ mm. at 21°, $h_2 = 360$ mm., $B = 751.8$ at 15°.

Calculated for $CH_3—CO—C(COOC_2H_5)_3$.	 For $CH_3\text{-}\overset{OCOOC_2H_5}{\overset{\vert}{C}}\text{-}CH\text{-}COOC_2H_5$.	Found.
274	202	200

Nef obtained his carb-ethoxyl-acet-acetic ether in a perfectly pure state by finally treating it with fuming nitric acid. Although I fail to understand why this operation is necessary, or even desirable, it was repeated, using a product which was already perfectly pure. 20 grams of the ether were gradually introduced into one and a half times its volume of fuming nitric acid (1.52), cooled off in a mixture of ice and salt, allowed to stand twenty minutes, during which time the escape of colored fumes was noticed, and then the solution thrown into ice-water. The oil which settled was separated from the supernatant liquid, water added to it, and then extracted with ether.[1] The ether solution was extracted three times with aqueous sodium carbonate (dilute sulphuric acid, added to this solution after extraction, gave fumes of nitrous acid), then three times with dilute potassium hydrate, finally once with water, and the ethereal solution dried over fused sodium sulphate. On fractionation, a product was obtained which boiled exactly at the same temperature as before this treatment, viz. 136° at 20 mm. pressure. I wish to correct here the statement made by Nef that carb-ethoxyl-acet-acetic ether is entirely unacted on by fuming nitric acid in the cold, as only 14 grams of the 20 used in the experiment were recovered, and on subjecting this product to a second treatment with fuming nitric acid it undergoes again a partial decomposition.

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[1] Nef extracts directly with ether — obviously a mistake, as the products of decomposition may be extracted along with the carb-ethoxyl-acet-acetic ether.

On analysis this supposed purer product gave the following result:

0.2317 gram substance gave, burned with $PbCrO_4$, 0.4551 gram CO_2 and 0.1532 gram H_2O.

	Calculated for $CH_3—\dot{C}OCOOC_2H_5—\dot{C}H—COOC_2H_5$.	Found.
C	53.46	53.56
H	6.93	7.22

A vapor-density determination of this product was also made, according to the vacuum method of Hofmann, with the following results: $p = 0.0457$, $v = 64.2$ cc., $h_1 = 325$ mm. at 22°, $h_2 = 347$ mm., $B = 753.3$ mm. at 15°, from which results the molecular weight 200.6 is calculated. It may safely be inferred from the above results that the treatment of carb-ethoxyl-acet-acetic ether with nitric acid is superfluous, entailing as it does only a considerable loss of substance. The statement made by Nef in regard to the formation of acet-malonic ether in the action of chlorcarbonic ether on sodium acet-acetic ether I have found correct. although in my experiment it was far less than the amount he obtained. Unfortunately a small part of this substance was lost through an accident and I am therefore unable to state exactly the proportion formed, but I am sure that 10 per cent. is certainly rather above than below the amount.

In the introduction to his paper Nef[1] expressed his opinion that my conclusion in regard to the constitution of carb-ethoxyl-acet-acetic ether is very doubtful, as all that was known about the compound was its neutral behavior towards alkalies and that it could be decomposed by alcoholic potash into acetone and carbonic acid. This critic showed by such statements how carelessly he had read my paper, for in it he would have found part of the results which he published as new.

Ten grams carb-ethoxyl-acet-acetic ether were cooled off in ice and 3.4 grams powdered dry sodium ethylate, in proportion of equal molecules, added in small quantities at a time, as otherwise the reaction is quite violent, and the mixture well stirred after

[1] Ann. Chem. (Liebig) **266**, 57.

each addition. The product became very thick, even before all the sodium ethylate was in the flask, and to facilitate the action finally a small quantity of dry ether was added and the almost solid mass mixed as well as possible. After standing in a cold place for a day, water was added to the product, and as soon as the solid had dissolved the solution was extracted with ether. After drying over fused sodium sulphate the ethereal extract was fractionated and, after one gram of liquid boiling between 125°–135° passed over,—which contained carbonic ether as was shown by decomposing it by caustic potash—the thermometer rose rapidly to 178° (only 0.15 gram liquid passed over between these temperatures) when 4 grams acet-acetic ether distilled off. The thermometer then rose rapidly to 235°–240° when 1.7 grams undecomposed carb-ethoxyl-acet-acetic ether passed off, leaving a very small black residue in the boiling-flask. On acidulating the alkaline liquid, which had been extracted by ether, considerable carbon dioxide was evolved, and from the acid solution a very small quantity of an oil was extracted, but the amount, 0.05 gram, did not permit a further examination. Carb-ethoxyl-acet-acetic ether is therefore decomposed by dry sodium ethylate into sodium carbonate, some carbonic ether and acet-acetic ether. After reading Nef's paper I repeated this experiment, as I inferred from his statement that an almost quantitative decomposition into ethyl carbonate and sodium acet-acetic ether takes place in this reaction, and as the results of the second experiment confirmed those I had previously obtained, the equation given by Nef[1] therefore does not represent the reaction correctly.[2]

In my first paper I mentioned that phenylhydrazine acetate and hydroxylamine act on carb-ethoxyl-acet-acetic ether, and that a solid product was obtained by using the first-named reagent. This reaction was examined shortly afterwards with the following results: To an aqueous solution of 10 grams phenylhydrazine chlorhydrate and 15 grams sodium acetate, 10 grams carb-ethoxyl-acet-acetic ether and sufficient alcohol to effect its solution were added. After standing some hours an oil began to separate from the solution. This gradually increased in quantity for several days, when the solution was extracted with ether, the extract dried over calcium chloride and then evaporated *in vacuo*. On

[1] Loc. cit. 107.

[2] By using alcoholic sodium ethylate proportionately less carbonic ether is formed.

long standing *in vacuo* the residue gradually turned almost solid, and was first digested in the cold with about 20 cc. dry ether, and an insoluble residue filtered off, which was then extracted twice with the boiling solvent. On cooling the last two extractions, needles separated, which were filtered off and added to the insoluble part, and the ether extracts evaporated, when on standing *in vacuo* the residue became almost solid. It was again treated with a small quantity of ether, filtered from a few crystals, and, after evaporation of the ether, the residue crystallised five times from carbon disulphide. Long white needles were obtained which melt at 80°–81°, and are sparingly soluble in cold water, moderately soluble in cold, readily in boiling carbon disulphide, and very soluble in cold alcohol or ether. On analysis the following results were obtained:

I. 0.1355 gram substance gave 0.2953 gram CO_2 and 0.0845 gram H_2O.

II. 0.2158 gram substance gave 29.8 cc. N at 16° and 753 mm. pressure.

III. 0.2013 gram substance gave 27.2 cc. N at 13° and 746.7 mm. pressure.

	Theory for $C_6H_5—NH—NHCOOC_2H_5$.	Found. I.	II.	III.
C	59.99	59.46	...	...
H	6.66	6.91	...	...
N	15.55	...	15.81	15.77

The crystalline, insoluble residue from the above product was purified by several crystallisations from water, and consisted of white prisms that melt at 127°, that agreed in all their physical and chemical properties with phenyl-methyl-pyrazolone. As the appearance of this compound may have been due to the formation of acet-acetic ether, it seemed of interest to ascertain whether that compound gives the pyrazolone with phenylhydrazine acetate. On allowing an alcohol solution of the ether and acetate to stand several days, then evaporating the alcohol *in vacuo*, a crystalline residue was obtained that dissolved in water and gave a very good yield of phenyl-methyl-pyrazolone on careful neutralisation. Knorr[1] had previously noticed the formation of this pyrazolone by heating an acetic-acid solution of hydrazine and acet-acetic ether, but attributed its formation to the action of heat on the "hydrazone."

[1] Ann. Chem. (Liebig) **238**, 147.

Nef[1] obtained the compound melting at 81° by the action of free phenylhydrazine on carb-ethoxyl-acet-acetic ether, and believes that two molecules of it to one of acet-acetic ether are formed in the reaction; and he also noticed the formation of water. My observations on the formation of the compound indicated that its presence was rather due to a secondary reaction. I therefore made an experiment on the action of the free base after reading Nef's paper. Five grams pure carb-ethoxyl-acet-acetic ether were dissolved in 5 grams dry ether and 2.55 grams phenylhydrazine (in proportion of equal molecules) were added. The solution became only perceptibly warm, and gradually took a yellow-brown color, but it remained perfectly clear. Nef's observation in regard to the formation of water in this reaction is incorrect, and the addition of calcium chloride, which was used to facilitate the formation of water, is quite unnecessary. Nef washed the ethereal solution with alkaline and acid solutions, but I shall show farther on that this treatment is not desirable, as both acids and alkalies act on hydrazones of β-ketone acid ethers. After standing four days the ether was evaporated and the residue allowed to stand in a vacuum as long as the crystals that soon separated increased in number. By adding petroleum ether and warming the greater part of the oil dissolved, and the remaining crystals, afterwards crystallised from as little hot carbon disulphide as possible and dried, weighed 1.6 grams and melted at 76°–78°. After several recrystallisations from carbon disulphide they melted at 80°–81° and agreed in their properties with the above-described compound.

The petroleum ether from the crystals was evaporated and allowed to remain several weeks *in vacuo*, but no further separation of crystals was noticed, and it may therefore be assumed that the amount above stated (1.6 grams) represents approximately the quantity of the substance that is formed in the reaction, which should be no less than 6.5 grams if Nef's view were correct. On treating the oil with alkalies it could be separated into a soluble and insoluble portion, neither of which could be obtained in a pure state, but no acet-acetic ether could be detected in the soluble part. Free phenylhydrazine acts, therefore, on carb-ethoxyl-acet-acetic ether forming an acid and a neutral substance, and the compound melting at 81°; but, as the amount of the latter substance formed is comparatively small, the other products may result from the direct action of the base with the elimination of alcohol.

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[1] Ann. Chem. (Liebig) **266**, 107.

Several experiments were made on the action of an alcoholic solution of hydroxylamine on carb-ethoxyl-acet-acetic ether, but as only a dark-colored oil was obtained which could not be purified, the reaction was not further studied.

The formation of the compound $C_6H_5NH—NH—COOC_2H_5$ by the action of phenylhydrazine acetate solution is of importance, as hitherto no instance is known where this mixture splits off carb-ethoxyl from derivatives of acet-acetic ether when this group is joined to carbon, whereas free hydrazine often acts as a base in such compounds. The above reaction is therefore a further proof of the constitution I originally assigned to carb-ethoxyl-acet-acetic ether, and indeed there is no property of the compound known which does not directly follow from such a structure.

Action of Acetyl Chloride on Sodium Malonic Ether.

This reaction was first studied by Lange,[1] who supposed the product he obtained to be identical with the neutral compound Conrad and Guthzeit had prepared by the action of chlorcarbonic ether on sodium acet-acetic ether.

In preparing this compound 7.2 grams finely granulated sodium were brought under 250 grams dry ether, and 50 grams malonic ether added in small quantities at a time. After no more hydrogen was evolved, even though the thick mass of sodium malonic ether was thoroughly shaken, the mixture was cooled off and 24.5 grams acetyl chloride added slowly from a drop-funnel. A reaction took place immediately, and, after a comparatively small amount of chloride had been added, the sodium derivative went into solution. On standing over night the solution showed a neutral reaction. About one-half of the ether was then distilled off, the remaining solution extracted with water, dried over calcium chloride, and, after the ether was driven off on a water-bath, the oil was fractionated *in vacuo*, as distillation under ordinary pressure caused considerable loss by decomposition. It was easy to separate three different liquids from the product of the reaction,—unchanged malonic ether, an oil boiling at 120° under 17 mm. pressure, and a higher-boiling liquid, the formation of which had been overlooked by Lange. Analyses of the product boiling at 120° gave the following numbers:

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[1] Ber. d. chem. Ges. **20**, 1325.

I. 0.1842 gram oil, burnt in open tube, gave 0.3591 gram CO_2 and 0.1215 gram H_2O.

II. 0.2640 gram oil, burnt with $PbCrO_4$, gave 0.5182 gram CO_2 and 0.1880 gram H_2O.

	Calculated for $CH_3-CO-CH(COOC_2H_5)_2$.	Found. I.	II.
C	53.46	53.16	53.51
H	6.93	7.22	7.16

Acet-malonic ether boils with slight decomposition under ordinary pressure, but without change *in vacuo.* It possesses strongly developed acid properties, dissolving readily in aqueous alkalies and even in aqueous solutions of alkaline carbonates, and is precipitated unchanged by addition of mineral acids. It is, however, gradually decomposed in an alkaline solution, as may be seen from the following experiment: one-half gram potassium hydrate (theory 0.45) was dissolved in 5 grams water and 2 grams of the ether added; but it was finally found necessary to add 0.2 potassium hydrate more before all the oil dissolved. On standing several hours some oil separated from the solution. This, however, dissolved again on addition of a small amount of potassium hydrate. The solution was then acidified, the solution extracted with ether, and only one gram acet-malonic ether was recovered by fractionation *in vacuo.* This decomposition was not studied any further, but a corresponding experiment with acet-ethylmalonic ethers makes it very probable that malonic and acetic acids or ethers are formed.[1] The sodium derivative was made by dissolving 0.35 gram sodium in 5 grams absolute alcohol and adding 3 grams ether. The solutions heated when mixed, and soon solidified to a mass of white prismatic plates, which are very soluble in water, pretty soluble in alcohol and sparingly in ether. It is also but slightly soluble in concentrated caustic potash, and may therefore be obtained by adding acet-malonic ether to such a solution.

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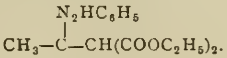
[1] Conrad and Brückner (Ztschr. phys. Chem. **7**, 290), in remarking on the saponification of malonic ether by sodium ethylate, state that these results are directly contrary to their own, but I fail to see that they are justified in such a conclusion. Acet-malonic ether acts as a well-marked acid substance, and it is not in the least surprising that its sodium derivative shows considerable stability. However, in mentioning that the ether dissolves unchanged in alkalies, I had no intention of asserting that the amount precipitated on adding acid is exactly that originally taken, but I am sure if it is decomposed at all it is only to a very slight extent. I do not feel at all certain whether these chemists have the same compound in view, as they still think that the neutral carb-ethoxyl-acet-acetic ether is acet-malonic ether, to judge from what they state in another part of their paper (page 284).

0.4610 gram vacuum-dried salt, which did not change in weight at 100°, gave 0.1492 gram Na_2SO_4.

	Theory for $CH_3{-}\dot{C}ONa{-}\dot{C}(COOC_2H_5)_2$.	Found.
Na	10.27	10.48

The presence of carbonyl was proven in acetyl-malonic ether by the formation of a phenylhydrazine derivative. Three grams ether were added to an aqueous solution containing equal weights of phenylhydrazine chlorhydrate and sodium acetate, and sufficient alcohol to effect solution was added. After standing a day, water was added to the solution, when a yellow crystalline precipitate fromed, which was purified by crystallising from alcohol, and an analysis gave the following result:

0.2449 gram substance gave 21 cc. nitrogen, $t=14°$, $B=766$ mm.



	Calculated for $CH_3{-}\overset{N_2HC_6H_5}{\overset{|}{C}}{-}CH(COOC_2H_5)_2$.	Found.
N	9.58	10.17

The hydrazone or hydrazo-derivative crystallises as white prismatic plates which are insoluble in cold water, pretty soluble in cold, easily in hot alcohol, and melt at 119°–121°.[1]

An alcoholic solution of hydroxylamine also acts on acetylmalonic ether, forming a thick oil, but, as it could not be purified by fractionation, even *in vacuo*, it was not further examined.

The higher-boiling product formed in the action of acetyl chloride on sodium malonic ether gave the following figures on analysis:

0.1698 gram substance, burnt with $PbCrO_4$, gave 0.3363 gram CO_2 and 0.0994 gram H_2O.

0.2158 gram substance, burnt with $PbCrO_4$, gave 0.4284 gram CO_2 and 0.1305 gram H_2O.

	Theory for $(CH_3CO)_2{=}C{=}(COOC_2H_5)_2$.	Found.	
		I.	II.
C	54.09	54.01	54.16
H	6.56	6.51	6.72

Diacet-malonic ether decomposes when boiled under ordinary pressure, which is the reason its formation was overlooked by Lange, but it can be distilled with but slight decomposition *in vacuo*, boiling at 156° under 17 mm. pressure (oil-bath 185°). It behaves as a neutral oil towards caustic alkalies, only dissolving in them with decomposition on standing.

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[1] Free phenylhydrazine appears to act differently. An ethereal solution deposited some crystals which are probably acetyl-phenyl-hydrazide, and the solution gave an oil that gradually solidified, but this substance is not identical with that above described. I shall examine this reaction more carefully.

Free phenylhydrazine acts readily on the ether, forming β-acetyl-phenyl-hydrazide. To a solution of 1.4 grams substance in 6 grams dry ether, 2.1 grams phenylhydrazine (2 mols.) were added and the mixture cooled in ice. After a few minutes a crystalline substance was deposited, which increased on standing, and which was filtered after two days. This precipitate was crystallised several times from alcohol and formed flat prisms with obliquely truncated end-faces that began to soften at 127° and melted at 127.5°–128°. These are properties that agree with those given by Fischer[1] for β-acetyl-phenyl-hydrazide, and the following analysis confirms the formation of that body:[2]

0.1526 gram substance, dried at 100°, gave 0.3826 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_6H_5—NH—NHCOCH_3$.	Found.
C	64.00	64.18
H	6.66	6.98

Action of Chlorcarbonic Ether on Sodium Malonic Ether.

Conrad and Guthzeit[3] described methin-tricarbonic ether, which they obtained by the action of chlorcarbonic ether on sodium malonic ether in presence of benzene, as a neutral substance, not capable of forming a sodium derivative. As such properties are not in accordance with those indicated by the constitution of methin-tricarbonic ether it seemed of interest to prepare and re-examine the substance.

To 8.7 grams granulated sodium, under 300 grams dry ether, 60 grams malonic ether were added and, after no more hydrogen was given off, 40.4 chlorcarbonic ether gradually allowed to drop into the mixture. A reaction took place immediately, but it was not as energetic as in the corresponding experiment with sodium acet-

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[1] Ann. Chem. (Liebig) **190**, 130.

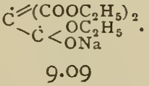
[2] Although the constitution $(CH_3CO)_2=C=(COOC_2H_5)_2$ for diacetyl-malonic ether is probable, there is as yet no strict proof for it, as the compound may be $CH_3—CO(OCCH_3)—C=(COOC_2H_5)_2$, which should be a neutral body and also give acetyl-phenyl-hydrazide with phenylhydrazine. This applies to diacet- and dibenzoyl-acet-acetic ethers, and I shall examine the behavior of these substances towards the phenylhydrazine acetate solution, as it will be shown further on that this reagent gives a hydrazone with compounds from which free phenylhydrazine splits off acetyl, forming acetyl-phenyl-hydrazide.

[3] Ann. Chem. (Liebig) **214**, 31.

acetic ether. After standing twelve hours the odor of chlorcarbonic ether was no longer noticeable, and the solution was heated for an hour with an inverted cooler, after cooling extracted with water and the ether solution dried over sodium sulphate. On fractionation *in vacuo* of the oil remaining when the ether was distilled off, besides malonic and methin-tricarbonic ethers no other product could be isolated. The compound boils unchanged at 137°–138° (17 mm. pressure, bath 160°), solidifying on cooling in large crystals melting at 28°, and agrees in all its physical properties with the compound described by Conrad and Guthzeit. In its chemical behavior, however, I found a very marked difference, since, instead of being neutral towards aqueous alkalies it dissolved readily in them, even in aqueous sodium carbonate, and was precipitated again by the addition of a mineral acid. Instead of decomposing easily on contact with sodium ethylate it formed at once a sodium derivative. 0.5 gram sodium was dissolved in 5 grams absolute alcohol and 5 grams ether, dissolved in an equal weight alcohol, added while cooling, when the liquid soon solidified to a mass of white crystals. After standing several hours the precipitate was filtered out, washed with dry ether and dried *in vacuo*. The sodium derivative is readily soluble in water, and mineral acids precipitate methin-tricarbonic ether from this solution. The sodium estimations of this substance gave the following results:

0.3838 gram sodium compound dried *in vacuo* gave 0.1078 gram Na_2SO_4.

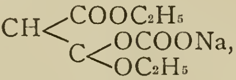
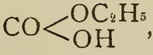
0.3671 gram sodium compound dried *in vacuo* gave 0.1025 gram Na_2SO_4.

	Theory for  $\dot{C}{\genfrac{}{}{0pt}{}{\diagup\!\!\diagup(COOC_2H_5)_2}{\diagdown\dot{C}<{OC_2H_5 \atop ONa}}}$.	Found.	
		I.	II.
Na	9.09	9.12	9.04

In view of the differences between the observations of Conrad and Guthzeit and my own on this product, it seemed hardly possible that we could have obtained the same compound, and I therefore prepared methin-tricarbonic ether according to their directions, by allowing chlorcarbonic ether to act on dry sodium malonic ether suspended in benzene. To 40.8 grams sodium malonic ether, prepared by adding the calculated amount of dry and finely powdered sodium ethylate to malonic ether while cooling, mixing well with a pestle, and drying *in* *vacuo* to constant weight, 100 grams dry benzene and then gradually 24.4 grams chlorcarbonic ether, diluted with three times its volume of benzene, were added. The mixture was then heated three hours, when the reaction was completed, and after the usual operations the product distilled in a vacuum. From this experiment 10 grams almost pure malonic ether, about two grams of oil boiling between 110°–135° and 23 grams methin-tricarbonic ether were obtained. This ether agreed in all respects, both in its chemical and physical properties, with the product already described, and as I also obtained the same compound by the action of chlorcarbonic ether on a cold alcoholic solution of sodium malonic ether, no other explanation remains for the anomalous properties which Conrad and Guthzeit ascribe to methin-tricarbonic ether than that their observations regarding its neutrality and the non-formation of a sodium derivative were not correct.

An attempt was made to introduce ethyl into methin-tricarbonic ether according to the Conrad-Limpach method. The alcoholic solution remained strongly alkaline, even after standing ten hours, and it was then heated to 100°, when it gradually became neutral. The product, worked up in the usual manner, was distilled *in vacuo*, and yielded an oil which boiled at from 202°–204° under ordinary pressure. This consisted of ethyl-malonic ether. It seemed of interest to determine whether potassium malonic ether would also give solely methin-tricarbonic ether. 2.45 grams granulated potassium were brought under 40 grams dry ether and 10 grams malonic ether added gradually. A violent reaction took place with formation of the potassium derivative, but even after standing ten hours and shaking it was found impossible to convert all the malonic ether into its potassium compound, as only 600 cc. hydrogen were given off, instead of 700 cc., which should be formed from the amount of potassium taken. To this mixture 6.7 grams chlorcarbonic ether, diluted with twice its volume dry ether, were slowly added, and the product after standing 10 hours showed a neutral reaction and was worked up as described above. By fractional distillation *in vacuo* unchanged malonic ether and methin-tricarbonic ether were isolated; the latter compound dissolved completely in dilute caustic potash, and, in fact, the formation of a neutral compound other than malonic ether could not be detected.

Behavior of Carbon Dioxide towards Sodium Malonic and Acet-acetic Ethers.

According to a preliminary note,[1] carbon dioxide acts on sodium malonic ether, in alcoholic solution, with formation of the compound $CH<^{COONa}_{(COOC_2H_5)_2}$, which decomposes in contact with water into malonic ether and sodium bicarbonate. Such a compound may have the constitution  $CH<^{COOC_2H_5}_{C<^{OCOONa}_{OC_2H_5}}$, which would explain the facility with which it is decomposed by water. In order to prove which of these two structures is correct I wished to replace the sodium by ethyl and compare the compound thus obtained with methin-tricarbonic ether; but, although the conditions were varied, I have not been able to repeat my original experiments with the same result. On passing carefully dried carbon dioxide into an absolute alcoholic solution of sodium malonic ether while cooling, the formation of a white precipitate occurred, but this precipitate, in my later experiments, always consisted of sodium ethyl-carbonate and dissolved perfectly in water, while previously the precipitate gave malonic ether, although it had been washed with alcohol and dried well between layers of filter-paper. It would seem as if under certain conditions, which I have not been able to ascertain, the described compound is formed, while under other, probably the usual ones, the carbon dioxide dissolving in alcohol forms unstable  $CO<^{OC_2H_5}_{OH}$, which acts on sodium malonic ether, setting free malonic ether and forming sodium ethyl-carbonate.

As the presence of alcohol interfered, some experiments on the action of carbon dioxide on sodium malonic ether suspended in ether were made. The sodium malonic ether was prepared by the action of granulated sodium on malonic ether dissolved in 15 times its volume of ether, care being taken to exclude water as far as possible, and through the thick mass, well cooled off in ice, carbon dioxide, dried first with sulphuric acid and then over phosphoric anhydride, was passed. It was noticed that the carbon dioxide was almost completely absorbed at first, and at the same time the sodium malonic ether began to go into solution. After passing a slow current of carbon dioxide about an hour a clear solution was obtained, when the gas went through unabsorbed. This solution, on standing in a closed vessel, deposits a very little of a gelatinous substance, but the quantity was too small to permit an examination. The ethereal solution was examined as to its behavior towards water, ethyl iodide and chlorcarbonic ether. When extracted with water sodium carbonate goes into solution, and from the ether solution malonic ether was separated by fractionation *in vacuo*. To another portion a slight excess of ethyl iodide was added and the mixture allowed to stand at ordinary temperature for a week. The ether solution still showed a decided alkaline reaction, although the formation of considerable sodium iodide showed that a reaction had taken place, and it was then heated some hours at 50°. After the usual treatment and fractionation *in vacuo* malonic and ethylmalonic ethers were isolated. A third portion was treated with chlorcarbonic ether, and after the reaction was completed malonic and methin-tricarbonic ethers were isolated from the liquid. From these results it would seem that there was still some unchanged sodium malonic ether in the ethereal solution, but that a part of the sodium derivative had undergone some change appears almost beyond question, as the solubility of carbon dioxide in ether is too small to cause the very considerable amount of sodium malonic ether to dissolve, and, besides, a very considerable amount of the gas had itself dissolved. It certainly seems as if carbon dioxide acts on sodium malonic ether to form an unstable sodium compound which is quite soluble in ether, a fact which precludes the formation of ethyl-sodium carbonate in the reaction, as this does not dissolve easily in ether. The compound evidently decomposes readily, since the ethereal solution evaporated *in vacuo* leaves a solid substance which is quite insoluble in ether. I shall continue the examination of this peculiar reaction, and hope my further work will throw more light on it.

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[1] This Journal **9**, 126.

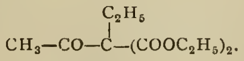
That carbon dioxide really acts on sodium malonic ether in presence of ether is further confirmed by its behavior towards sodium acet-acetic ether under exactly the same conditions. In this case there is no absorption of the gas, and, no matter how long it is passed through the mixture, the sodium acet-acetic ether does not dissolve nor is it changed.

Action of Acetyl Chloride on Sodium Ethyl-malonic Ether.

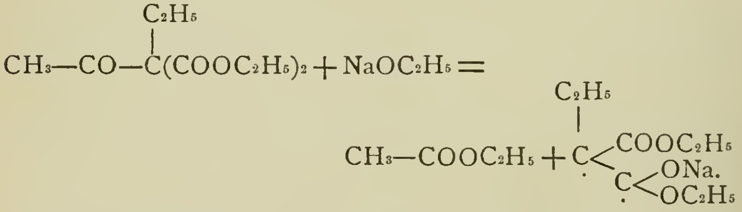
To 5.7 grams granulated sodium under 100 grams dry ether 46 grams ethyl-malonic ether—a product boiling between 205°–206° was fractionated *in vacuo*, when it boiled at 104°–105° under 20 mm. pressure—were gradually added. Before quite all the ether was added a white precipitate of the sodium derivative began to separate, but the greater part of the sodium was already in solution. The mixture was allowed to stand at ordinary temperature for some hours and repeatedly shaken. After the evolution of hydrogen had entirely ceased, the flask was cooled in ice-water and 19.5 grams acetyl chloride slowly added, while shaking the flask. The precipitate of sodium ethyl-malonic ether dissolved after a small quantity of acetyl chloride had been added. After standing ten hours in ice-water the liquid had become yellowish and showed a very slight acid reaction. It was then shaken out with water (the use of alkalies must be avoided, as the compound formed is decomposed even in ethereal solution by contact with aqueous alkalies), the ether solution dried over sodium sulphate and heated in a water-bath until no more ether went off. The residue was then fractionated *in vacuo*, an operation which was repeated ten times, as a considerable quantity of the acet-ethylmalonic ether goes over in the first fractionations above the correct boiling-point. From this experiment 19 grams of an oil boiling unchanged at 137°–137½° under 20 mm. pressure, 4 grams of the same product boiling at 136°–138° (20 mm.), about 4 grams of a liquid that went over 115°–118° which has not been further examined, some unchanged ethyl-malonic ether and a small quantity of a higher-boiling product—between 150°–160° at 20 mm.—but not in sufficient amount to purify by further fractionation, were obtained. Acetic acid was also found in the original aqueous extract. The principal product of the reaction was analysed with the following results:

0.1648 gram substance, burnt with $PbCrO_4$, gave 0.3458 CO_2 and 0.1173 H_2O.

0.1581 gram substance, burnt with $PbCrO_4$, gave 0.3320 CO_2 and 0.1035 H_2O.

	Theory for  $CH_3{-}CO{-}\overset{C_2H_5}{\overset{\vert}{C}}{-}(COOC_2H_5)_2$.	Found.	
		I.	II.
C	57·37	57·23	57·32
H	7.82	7·91	7·98

Acet-ethyl-malonic ether forms a colorless oil which boils at 137°–137½° under 20 mm. pressure (bath 165°), and is sparingly soluble in water, readily in alcohol and ether. It behaves towards alkalies as a neutral body, a property in accordance with its constitution, but undergoes, even with aqueous alkalies, a decomposition very easily, to form an acetate and an ethyl-malonate. This reaction may also be effected by continued shaking of an ethereal solution of the compound with aqueous potash, when it is gradually completely decomposed, and the alkaline solution then contains potassium acetate and ethyl-malonate, while the ethereal solution contains a very considerable amount of ethyl-malonic ether. On adding the calculated quantity of sodium ethylate (dried at 200° in hydrogen) to acet-ethyl-malonic ether cooled off in ice, a reaction took place immediately, and the ethylate dissolved in the ether to form an amber-colored liquid, which smelt strongly of acetic ether. The mixture stood in the cold a day and was then dissolved in cold water and extracted with ether. After drying over sodium sulphate the ethereal solution was fractionated, and not far from the calculated quantity of ethyl-malonic ether, besides some acetic ether, was isolated. The aqueous solution gave off no carbon dioxide on acidulating, and contained some acetic and ethyl-malonic acids:



$$CH_3{-}CO{-}\overset{\overset{\large C_2H_5}{|}}{C}(COOC_2H_5)_2 + NaOC_2H_5 = CH_3{-}COOC_2H_5 + \overset{\overset{\large C_2H_5}{|}}{C}{<}\begin{matrix}COOC_2H_5\\ C{<}\begin{matrix}ONa.\\ OC_2H_5\end{matrix}\end{matrix}$$

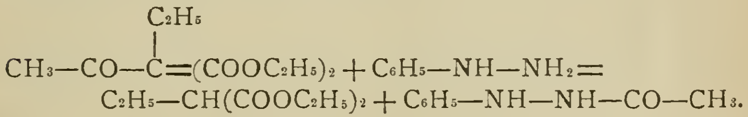
Free phenylhydrazine acts readily on the body, forming acet-phenyl-hydrazide. 4 grams substance were dissolved in 3 grams dry ether, and 1.9 grams phenylhydrazine added to the solution. No heat was perceptible, nor was any water formed in the reaction, but in about an hour long crystals began to separate, which increased in number until the solution appeared almost solid. After standing 36 hours the crystals were filtered, washed with a little ether, and weighed 2.3 grams after drying in the air. The crude product melted at 123°–125°, but after several crystallisations from alcohol the melting-point remained constant at 127.5°–128.5°.

The substance has all the properties noted by Fischer[1] for the compound $C_6H_5—NH—NH—CO—CH_3$, the formation of which was confirmed by the following analysis:

0.1317 gram substance gave 0.3100 gram CO_2 and 0.0827 gram H_2O.

	Calculated for $C_6H_5—NH—NHCOCH_3$.	Found.
C	64.00	64.15
H	6.66	6.97

On evaporation of the ethereal filtrate an oil was obtained that gave a few more crystals of the hydrazide on standing in a vacuum. It was not further examined, but probably consisted largely of ethyl-malonic ether, as the hydrazide obtained was almost in theoretical quantity; 2.3 grams were obtained instead of the 2.5 grams that should be formed if the reaction takes place according to the following equation:



$$CH_3—CO—\overset{\overset{C_2H_5}{|}}{C}=(COOC_2H_5)_2 + C_6H_5—NH—NH_2 = C_2H_5—CH(COOC_2H_5)_2 + C_6H_5—NH—NH—CO—CH_3.$$

The facility with which acet-phenyl-hydrazide is formed appears indeed surprising in view of the ease with which these ketone-acid ethers form hydrazones with that reagent, but it is evidently a result of the loosening of the affinity of carbon to carbon by the accumulation of negative radicles on one carbon. It was of importance to bring a decided proof that acetyl in this compound is joined to carbon, as all the decompositions hitherto described accord also with the properties of an acetyl derivative in which it is joined to oxygen. That this is not the case, however, was shown by the preparation of the hydrazone of acet-ethyl-malonic ether. To 2 grams each of phenylhydrazine chlorhydrate and sodium acetate dissolved in 16 grams water, 2 grams of the compound and sufficient alcohol (20 grams) were added to form a clear solution, even when it was cooled to 0°. After several hours an oil began to separate, which increased in volume on longer standing, and was separated from the mother-liquor. It was dissolved in alcohol, precipitated by addition of water, this operation repeated and, after the mother-liquor was removed, the oil dissolved in ether, dried over sodium sulphate, filtered, and evaporated *in vacuo*. After standing several days the liquid had turned almost solid, and it was then pressed between filter-paper and washed a number of times with petroleum ether. As I found it impossible to recrystallise this substance, it was dried *in vacuo* and gave the following results for nitrogen:

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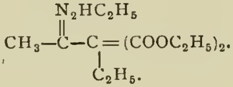
[1] Ann. Chem. (Liebig) **190**, 129.

0.1269 gram substance gave 10.2 cc. N at 13° and 759 mm. pressure.

0.2618 gram substance gave 19.8 cc. N at 15° and 756 mm. pressure.

	Theory for  $CH_3-\overset{\overset{\displaystyle N_2HC_2H_5}{\|}}{C}-\underset{\underset{\displaystyle C_2H_5.}{|}}{C}=(COOC_2H_5)_2.$	Found. I.	II.
N	8.75	9.49	9.17

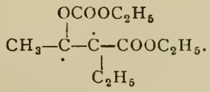
The hydrazone forms slightly yellowish, large prisms that melt at 44°–45°, and are soluble in the usual solvents with the exception of ligroin and petroleum ether. If allowed to stand in a desiccator over sulphuric acid it gradually turns into an oil, undergoing some chemical change, as it was found impossible to reconvert this oil into the solid substance.

Action of Chlorcarbonic Ether on Sodium Ethyl-acet-acetic Ether.

The ethyl-acet-acetic ether used in these experiments was made according to the Conrad-Limpach method and fractionated under ordinary pressure. This product was then extracted twice with dilute caustic potash to free it from a little acet-acetic ether which it is difficult to remove by fractionation, and the product then distilled twice *in vacuo*. It boils at 95° under 20 mm. pressure (bath 115°) without decomposition. To 8.2 grams granulated sodium under 125 grams dry ether 55.5 ethyl-acet-acetic ether were added from a drop-funnel, the mixture being kept cool in ice-water. When most of the ether had been added the contents of the flask turned thick, owing to the separation of the sodium derivative. The flask was removed from ice-water, repeatedly shaken and, when no more hydrogen was given off, again cooled off in ice and 38.5 chlorcarbonic ether added in small portions, while shaking the flask. The sodium derivative went into solution after a few grams of chlorcarbonic ether had dropped in, and the solution remained clear until the greater part of this reagent was added, when it began to take a gelatinous consistency. A test for sodium chloride at this point showed that a considerable proportion of the chlorcarbonic ether must have reacted with the sodium derivative. The mixture stood several hours in ice, then over night at ordinary temperature, but still showed an alkaline reaction, which did not disappear even on standing a day longer. It was then heated gently for a half-hour (after which it gave only a very faint alkaline reaction) and extracted twice with water. The solution was dried over sodium sulphate and, after removal of the ether, fractionated *in vacuo*. Besides some ethyl-acet-acetic ether there was only one other product formed. It was much easier to obtain this pure than the product in the corresponding experiment with sodium ethyl-malonic ether, and it was also obtained in a much larger yield. The above experiment gave 45 grams of oil boiling from 146° to 148° under 20 mm., 6 grams from 120° to 143°, but the thermometer did not stop at 138° and there was no indication of the formation of acet-ethyl-malonic ether; 3 grams from 143° to 146° and 8 grams from 148° to 152°, which undoubtedly consisted principally of the new body. After several fractionations in a vacuum a constant-boiling product was obtained, which was analysed with the following results:

0.1547 gram oil, *burnt in open tube*, gave 0.3219 gram CO_2 and 0.1118 gram H_2O.

0.1449 gram oil, burnt with $PbCrO_4$, gave 0.3060 gram CO_2 and 0.1040 gram H_2O.

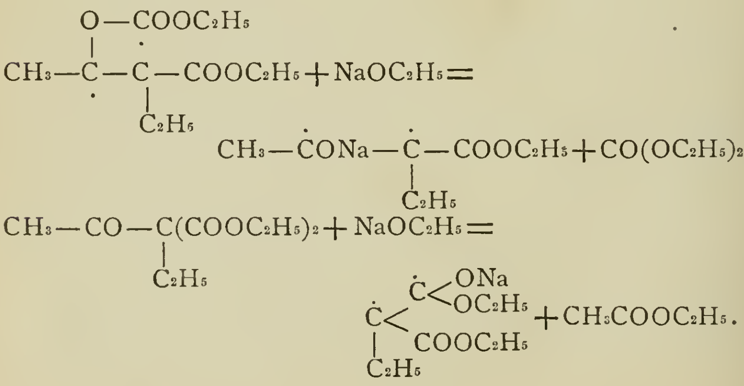
Theory for 

$CH_3-\overset{OCOOC_2H_5}{C}-\underset{C_2H_5}{C}-COOC_2H_5$.

	Theory	Found I.	Found II.
C	57.37	56.74	57.58
H	7.82	8.03	7.97

Carb-ethoxyl-ethyl-acet-acetic ether is a colorless oil that boils at 146° under 20 mm. pressure (bath 175°) with very slight decomposition, and is sparingly soluble in water, miscible with ether and alcohol. It acts as a neutral body towards aqueous solutions of alkaline carbonates and alkalies, but gradually undergoes decomposition in contact with them. The substance differs not only in its boiling-point from acet-ethyl-malonic ether, but also very characteristically in its behavior towards phenylhydrazine and sodium ethylate. To 6.8 grams substance, cooled in ice, 2 grams powdered sodium ethylate (which contained a little alcohol) were added, while stirring the mixture. A violent reaction took place, and, unless the flask was well cooled off, the contents of the flask became quite warm. After standing a few minutes a semi-solid, slightly yellow mass was formed and the decomposition was virtually completed. The mixture stood a day in a cool place and was then extracted with water. There was no odor of acetic ether noticeable, which was so marked in the corresponding experiment with acet-ethyl-malonic ether. After extracting with ether, drying the extract and fractionating, a small quantity of a liquid boiling at 125°–135° went over, when the thermometer rose very rapidly to 192°, and from that temperature to 198° three grams of ethyl-acet-acetic ether distilled off. The oil was shown to be ethyl-acet-acetic ether by conversion into a pyrazolone, according to a new method which I shall describe farther on. The portion boiling between 125°–135° contained a small quantity of carbonic ether, as, after treating it with alkalies and acidulating, carbon dioxide was given off, although the amount of carbonic ether formed was less than was obtained in decomposing carb-ethoxyl-acet-acetic ether. Above 198° a very small quantity of oil remained that did not pass over even when the metal bath was heated to 260°. This probably consisted of unchanged substance. The aqueous solution after extraction with ether, on addition of dilute sulphuric acid, gave off a very considerable quantity of carbon dioxide, and, on extracting with ether, a small quantity of propyl-methyl-ketone was obtained, evidently formed in the decomposition of ethyl-acet-acetic ether by the alkali.

Carb-ethoxyl-ethyl-acet-acetic ether, therefore, gives mainly ethyl-acet-acetic ether, carbon dioxide and carbonic ether when treated with sodium ethylate, while the isomeric acet-ethyl-malonic ether yields acetic acid and ethyl-malonic and acetic ethers:



$$CH_3—\underset{\cdot}{\overset{\overset{\displaystyle O—COOC_2H_5}{|}}{C}}—\underset{\underset{\displaystyle C_2H_5}{|}}{\dot{C}}—COOC_2H_5+NaOC_2H_5=$$

$$CH_3—\dot{C}ONa—\underset{\underset{\displaystyle C_2H_5}{|}}{\dot{C}}—COOC_2H_5+CO(OC_2H_5)_2$$

$$CH_3—CO—\underset{\underset{\displaystyle C_2H_5}{|}}{C}(COOC_2H_5)_2+NaOC_2H_5=$$

$$\underset{\underset{\displaystyle C_2H_5}{|}}{\dot{C}}<\begin{matrix}\dot{C}<\begin{matrix}ONa\\OC_2H_5\end{matrix}\\COOC_2H_5\end{matrix}+CH_3COOC_2H_5.$$

Quite as marked is the difference in the behavior of the isomers towards phenylhydrazine. Carb-ethoxyl-ethyl-acet-acetic ether was treated, under exactly the same conditions as already described with acet-ethyl-malonic ether, but in this experiment there was no crystalline deposit, even when the mixture stood several weeks. On evaporating the ether *in vacuo* and allowing the residue to remain there for some days it partially solidified, but did not become altogether solid, even on long standing. The product was filtered under pressure and the almost solid mass washed with carbon disulphide, in which the liquid dissolves, leaving a yellowish crystalline substance which was obtained pure by four crystallisations from that solvent. The substance melted at 81° and was in every respect identical with the product obtained by the action of phenylhydrazine on carb-ethoxyl-acet-acetic ether, a conclusion which was confirmed by the following estimation:

0.1237 gram substance gave 16.8 cc. N at 14° and 747 pressure.

	Theory for $C_6H_5N_2HCOOC_2H_5$.	Found.
N	15.55	15.79

The mother-liquor from the hydrazide was not further examined, but very probably contained some ethyl-acet-acetic ether and products formed by the action of phenylhydrazine on that compound. It may be mentioned that the amount of the hydrazide obtained is comparatively small for the quantity of substance used.

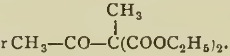
Preparation and Properties of Acet-methyl-malonic and Carb-ethoxyl-methyl-acet-acetic Ethers.

Although the above-described experiments with sodium acet-acetic and malonic ethers and their ethyl homologues make it very probable that the corresponding methyl derivatives are analogous compounds, it seemed of sufficient interest to make these experiments. In reactions depending on the relative negativity and positivity of the unsaturated carbons whether an addition or substitution takes place, any change in this relation may give rise to a somewhat different result; and, even though analogous results were obtained, these would be but desirable confirmations, as the synthesis of derivatives of acet-acetic ether in which the introduced radicle is joined to oxygen and not to carbon is certainly very anomalous.

The methyl-malonic ether used in the following experiment was prepared by quickly adding methyl iodide to sodium malonic ether kept cool in ice-water, and fractionating the product *in vacuo*. It was thought possible to avoid in this way the formation of methyl or mixed malonic ethers,[1] which are always formed in small quantity under the usual conditions, but, even after repeated fractionation of a product boiling perfectly constantly at 95.5° (corrected) under 20 mm. (bath 125°), the density determination of the product was $D = 1.028 \frac{15^\circ}{15^\circ}$, showing that it is not possible to obtain a perfectly pure product according to the Conrad-Limpach method.

The ether was converted into the sodium derivative by treating with granulated sodium in ethereal solution — a reaction which is more difficult to complete than that with ethyl-malonic ether, as the sodium derivative is somewhat less soluble in ether — the mixture cooled in ice, and the required amount of acetyl chloride added. The further treatment was like that described with the ethyl derivative, and by repeated fractionating *in vacuo* a pure product was isolated and analysed.

0.1860 gram substance, burned with $PbCrO_4$, gave 0.3792 gram CO_2 and 0.1300 gram H_2O.

	Theory for  $CH_3—CO—\overset{CH_3}{\overset{|}{C}}(COOC_2H_5)_2$.	Found.
C	55.55	55.59
H	7.40	7.80

Besides this compound, the only products that could be isolated were acetic acid and unchanged methyl-malonic ether. Acet-methyl-malonic ether boils without decomposition at 129.5°–130° (corrected, 131°–131.5°) under 20 mm. pressure (bath 160°), and is sparingly soluble in water, miscible with alcohol and ether. Like the ethyl compound it behaves as a neutral body towards alkalies, but is gradually decomposed by them. Dry sodium ethylate acted very readily on the ether in the cold, forming when first added white fumes, and soon a strong odor of acetic ether became noticeable. After standing some hours in ice-water the contents of the flask were treated with water, then acidulated and extracted with ether. From the ether-extract acetic acid and ethyl and methyl-malonic ethers were isolated by fractionation. A solution of one part acet-methyl-malonic ether in two parts dry ether and the equivalent quantity of phenylhydrazine soon deposits crystals, which increase in number on longer standing. These crystals were obtained pure by crystallising several times from alcohol, and melted at 127.5°–128.5°. All their properties agree with those of β-acet-phenyl-hydrazide, the formation of which was confirmed by a nitrogen estimation:

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[1] Perkin: J. Chem. Soc. 45, 510.

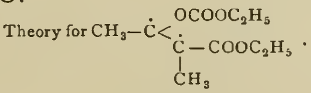
0.1196 gram substance gave 19 cc. N at 4.5° and 741 mm. pressure.

	Theory for $C_6H_5-NH-NH-CO-CH_3$.	Found.
N	18.6	19.0

With phenylhydrazine acetate solution a different product, probably a hydrazone, is formed, but the reaction was not further examined.

To prepare carb-ethoxyl-methyl-acet-acetic ether, chlorcarbonic ether was allowed to act on sodium methyl-acet-acetic ether in presence of ether, while cooling with ice, under the conditions already described with the ethyl derivative. By repeated fractionation *in vacuo* the product of the reaction was separated into comparatively little of an oil boiling at 120°–135°, which contained some carbonic ether, besides some unchanged methyl-acet-acetic ether, and about 50 per cent. of the theoretical quantity of the new ether, which was analysed with the following results:

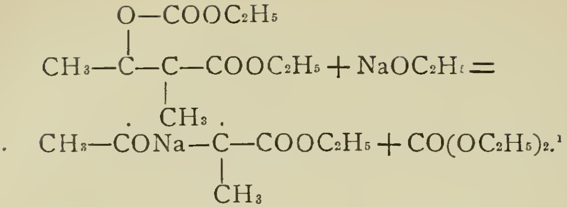
0.2138 gram oil, burnt with $PbCrO_4$, gave 0.4360 gram CO_2 and 0.1521 gram H_2O.



	Theory for $CH_3-\dot{C}<\begin{matrix}OCOOC_2H_5\\ \dot{C}-COOC_2H_5\\ \mid\\ CH_3\end{matrix}$.	Found.
C	55.55	55.63
H	7.40	7.85

Carb-ethoxyl-methyl-acet-acetic ether is a colorless oil, boiling at 136° (corrected, 137°) under 20 mm. (bath 160°). It is neutral in its behavior towards aqueous alkalies, but gradually undergoes decomposition when allowed to stand with such solutions.

Sodium ethylate (dried in hydrogen at 200°) acted readily on the ether cooled in ice, and white fumes formed in the flask. After thoroughly mixing and allowing the product to stand some hours it was worked up as already described, and considerable carbon dioxide, some carbonic ether and methyl-acet-acetic ether were obtained as decomposition-products:



$$CH_3{-}\overset{\displaystyle O{-}COOC_2H_5}{\overset{|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COOC_2H_5 + NaOC_2H_5 = CH_3{-}CONa{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COOC_2H_5 + CO(OC_2H_5)_2.^{1}$$

Towards phenylhydrazine it behaves like the corresponding ethyl derivative, the hydrazide melting at 80° and a heavy oil being the products of the reaction, but no acet-phenylhydrazide was formed.

Properties of Propionyl-malonic Ether.

This compound was prepared according to Lange's[2] directions, by the action of propionyl chloride on sodium malonic ether in presence of ether, and also by first preparing the sodium malonic ether by the action of sodium ethylate on malonic ether, and after drying in a vacuum, treating a mixture of the substance and ether as before. In either case, however, it is well to cool in ice during the reaction, as a somewhat better result is thereby obtained. The yield is comparatively small, a considerable quantity of malonic ether and a high-boiling liquid, undoubtedly dipropionyl-malonic ether, which decomposed when distilled under ordinary pressure, were formed. The re-formation of malonic ether is undoubtedly due to the action of propio-malonic on sodium malonic ether, as the former has a much stronger acid character than malonic ether and it therefore substitutes hydrogen for sodium.

Propio-malonic ether, like acet-malonic ether, acts as an acid towards aqueous solutions of alkaline carbonates and alkalies, dissolving in them without noticeable decomposition, and is precipitated on acidulation. The sodium derivative was obtained by adding dry sodium ethylate to the ether, kept well cooled in ice,

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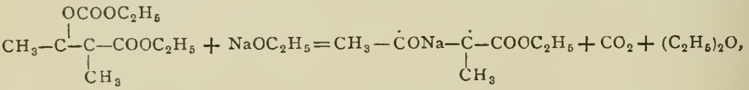
[1] In these experiments with sodium ethylate, carbon dioxide was formed in larger quantities than carbonic ether. It is possible that ether is formed as a direct product of the reaction, as it has been shown to be formed when sodium ethylate acts on organic ethers (Lossen and Köhler, Ann. Chem. (Liebig) **262**, 207). In this case its formation would be represented as follows:



$$CH_3{-}\overset{\displaystyle OCOOC_2H_5}{\overset{|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COOC_2H_5 + NaOC_2H_5 = CH_3{-}\dot{C}ONa{-}\underset{\displaystyle CH_3}{\underset{|}{\dot{C}}}{-}COOC_2H_5 + CO_2 + (C_2H_5)_2O,$$

or it may be formed secondarily by the action of sodium ethylate on carbonic ether:

$$CO(OC_2H_5)_2 + NaOC_2H_5 = CO{<}{}^{ONa}_{OC_2H_5} + (C_2H_5)_2O.$$

[2] Ber. d. chem. Ges. **20**, 1326.

when it solidified to a crystalline mass. This was pressed between filter-papers, washed with a little dry ether, and dried *in vacuo.*

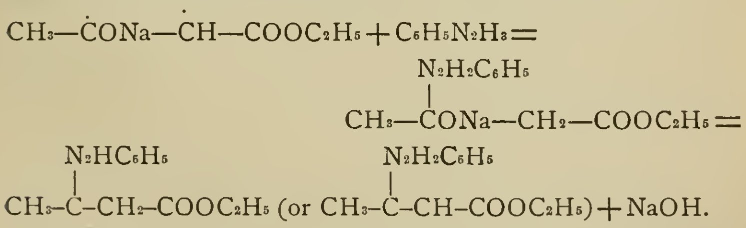
0.4173 gram substance gave 0.2224 gram Na_2SO_4.

	Calculated for $C_2H_5—\dot{C}ONa—\dot{C}—(COOC_2H_5)_2$.	Found.
Na	16.66	16.80

It dissolved readily in water to form a clear solution, and dilute sulphuric acid precipitated propio-malonic ether. If, however, the alkaline solution was allowed to stand, the ether gradually underwent decomposition.

Action of Phenylhydrazine on Sodium Acet-succinic Ether.

As phenylhydrazine acts readily on ethers of ketone acids forming hydrazones or hydrazo-products, it seemed of interest to ascertain whether their merotropic sodium derivatives would likewise give such compounds. Although the sodium derivatives do not contain a ketone-carbonyl, still hydrazones or hydrazo-products may be formed by addition of phenylhydrazine to the unsaturated carbons and subsequent elimination of sodium hydrate, a reaction which is represented by the following equations:



$$CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5 + C_6H_5N_2H_3 = CH_3—\overset{\overset{\displaystyle N_2H_2C_6H_5}{|}}{C}ONa—CH_2—COOC_2H_5 =$$

$$CH_3–\overset{\overset{\displaystyle N_2HC_5H_5}{|}}{C}–CH_2–COOC_2H_5 \text{ (or } CH_3–\overset{\overset{\displaystyle N_2H_2C_5H_5}{|}}{C}–CH–COOC_2H_5) + NaOH.$$

A few experiments in this direction have been made, beginning with acet-succinic ether, as its phenylhydrazine derivative had been obtained in a solid state and its sodium derivative is easily soluble in ether. The acet-succinic ether was prepared in the usual manner, but the crude product was distilled *in vacuo*, as I found with Gottstein[1] that it is impossible to obtain this compound pure by distillation under ordinary pressure. It passes over unchanged at 167°–168° under 35 mm. pressure (bath 195°).

10 grams of the ether were dissolved in 25 grams dry ether and 1.06 grams sodium added, of which all but a very small quantity finally went into solution. After removing the undissolved

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[1] Ann. Chem. (Liebig) **216**, 36; also Perkin: J. Chem. Soc. **45**, 517.

sodium, 5 grams phenylhydrazine were added and the solution allowed to stand five days. Only a very slight deposit had separated, and the solvent was removed by evaporation *in vacuo.* The residue was extracted with water, separated from some insoluble oil, and the aqueous alkaline liquid acidulated with acetic acid, when a crystalline precipitate was deposited. This precipitate dissolved almost completely in boiling water, and was separated from a small amount of insoluble liquid. The yellowish crystals were purified by several crystallisations from alcohol.

0.1262 gram substance, dried at 100°, gave 0.2858 CO_2 and 0.0629 H_2O.

0.2257 gram substance, dried at 100°, gave 23.3 cc. N, $t = 13°$, $B = 764$ mm.

	Theory for $C_{12}H_{12}O_3N_2$.	Found. I.	Found. II.
C	62.06	61.76	...
H	5.17	5.54	...
N	12.06	...	12.31

The new compound forms large white prisms that melt at 175°–177°, but begin to soften considerably below that temperature. They are sparingly soluble in hot ligroin, benzene and chloroform, somewhat more in cold water and hot chloroform, pretty easily soluble in hot water, alcohol and acetic ether. They are also soluble in caustic alkalies, and are precipitated unchanged by addition of acetic acid.

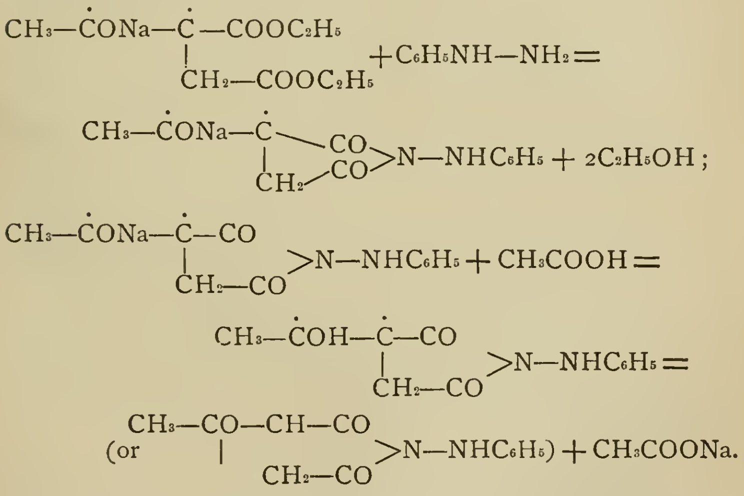
The sodium derivative formed in this reaction may be obtained by allowing phenylhydrazine to act on an absolute alcoholic solution of sodium acet-succinic ether, the substances being used in molecular proportions. If an excess of alcohol was avoided the solution solidified on standing to a mass of large prisms, which were filtered, washed with a very little absolute alcohol, then with ether and dried *in vacuo.*

0.3298 gram substance gave 0.095 gram Na_2SO_4.

	Calculated for $C_{12}H_{11}NaO_3N_2$.	Found.
Na	9.06	9.34

Heated to 100° it slowly decomposes, turning yellowish brown. It dissolves in water, and addition of acetic acid precipitates the substance melting at 173°–177°. The crude precipitate in the above experiment contained a second compound, which can be separated from it by extracting with water, in which it does not dissolve. This substance melted at 80°, and was identical with the "hydrazone" obtained by Knorr,[1] by the action of phenylhydrazine on free acet-succinic ether. The amount formed is, however, small in comparison to that of the sodium derivative, of which as much as 80 per cent. of the theoretical yield was obtained. The formation of this "hydrazone" could not be observed when ethereal sodium acet-succinic ether was employed, and it may be due to the presence of a small quantity of free acet-succinic ether, even though there was sufficient sodium ethylate to complete the reaction.

The compound $C_{12}H_{11}NaO_3N_2$ is formed from a molecule of acet-succinic ether and one of phenylhydrazine by the abstraction of two molecules of alcohol. The reaction and the constitution of the substance are very likely correctly represented by the following equations:



$$\begin{array}{l} CH_3-\dot{C}ONa-\dot{C}-COOC_2H_5 \\ \qquad\qquad\qquad | \\ \qquad\qquad\quad CH_2-COOC_2H_5 \end{array} + C_6H_5NH-NH_2 =$$

$$CH_3-\dot{C}ONa-\begin{array}{l} \dot{C}-CO \\ | \\ CH_2-CO \end{array}\!\!>N-NHC_6H_5 + 2C_2H_5OH;$$

$$CH_3-\dot{C}ONa-\begin{array}{l} \dot{C}-CO \\ | \\ CH_2-CO \end{array}\!\!>N-NHC_6H_5 + CH_3COOH =$$

$$CH_3-\dot{C}OH-\begin{array}{l} \dot{C}-CO \\ | \\ CH_2-CO \end{array}\!\!>N-NHC_6H_5 =$$

$$\left(\text{or } CH_3-CO-\begin{array}{l} CH-CO \\ | \\ CH_2-CO \end{array}\!\!>N-NHC_6H_5\right) + CH_3COONa.$$

Since phenylhydrazine reacts on free acet-succinic ether with great readiness even in the cold to form its "hydrazone," it certainly seems as if the formation of an entirely different product from sodium acet-succinic ether indicates different constitutions for the free ether and its sodium derivative, a fact which finds its best explanation in the merotropy of the two substances. It may appear, however, as if the sodium in sodium acet-succinic ether favored the formation of acet-succin-hydrazanil[1] instead of the "hydrazone," inasmuch as the latter substance has many less marked acid properties; but this explanation is not valid, as it will be shown further on that these "hydrazones" are unstable in presence of sodium ethylate or hydrate, they passing over into the corresponding pyrazolone, which class of compounds possess very decided acid properties and form stable sodium derivatives. A further confirmation of the above-stated view is found, I believe, in the behavior of sodium acet-succinic ether, in alcoholic solution, towards phenylhydrazine when the proportion of two molecules of the base to one of the sodium derivative is taken. Under these conditions a precipitate of the sodium acet-succin-hydrazanil appeared only after the solution had stood for some days, and, even after standing much longer, the quantity was not so great as when equal molecules were taken. This precipitate dissolved almost completely in water, and the solution gave acet-succin-hydrazanil on acidulating with acetic acid. The filtrate was evaporated in a vacuum, extracted with water (a small amount of solid did not dissolve, probably the "hydrazone") and gave an oil on acidulating with chlorhydric acid, which partially solidified on long standing, but the amount obtained did not permit further examination. I intend to repeat this experiment on a larger scale and examine it more thoroughly, although the formation of sodium acet-succin-hydrazanil in presence of an excess of phenylhydrazine is certainly strong evidence against the absence of a ketone-carbonyl in sodium acet-succinic ether. A number of experiments on the action of phenylhydrazine on the sodium derivatives of acet-acetic and ethyl-acet-acetic ethers have been made, but, as they are not completed, I shall return to this subject in a later paper.

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[1] Ber. d. chem. Ges. **17**, 2151.

A New Method of Converting Acet-acetic Ether and its Derivatives into Pyrazolones.

This interesting class of compounds was discovered by Knorr by heating the "hydrazones" of the ethers of β-ketone acids. The derivative of acet-acetic ether is converted with loss of alcohol at 100°, while its homologues require heating to a higher temperature. The above-described formation of phenyl-methyl-pyrazolone in the action of phenylhydrazine acetate on carbethoxyl-acet-acetic ether in the cold induced me to make a similar experiment with acet-acetic ether, and here too the same pyrazolone was obtained. According to E. Fischer[1] the presence of a free mineral acid interferes with the formation of hydrazones with aldehydes and ketones, prevents it in the case of levulinic and acet-acetic acids, but not with α-carbonyl acids. It has already been shown[2] that in using levulinic ether, instead of the free acid, a hydrazone is readily obtained, and the same difference seemed probable between acet-acetic acid and its ether.

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[1] I should like to suggest this name of hydrazanil for the derivatives of phenylhydrazine corresponding to the anils.

To a mixture of acet-acetic ether and phenylhydrazine chlorhydrate, the addition of three or four drops strong chlorhydric acid caused no apparent change, but when the flask was heated for a moment in a water-bath a reaction took place, the salt dissolving to form a clear solution, and alcohol and water vapors were given off. The time required to complete the reaction depends on the amount of the substance used, but ten or fifteen minutes' heating was generally sufficient. The contents of the flask were dissolved in water and carefully neutralised with dilute caustic soda, when an oil was precipitated which soon solidified. This substance after crystallising with alcohol melted at 127°, acted both as a base and an acid, and was identical with phenyl-methyl-pyrazolone obtained by Knorr on heating the "hydrazone" of acet-acetic ether at 100°. The yield obtained was almost the theoretical.

The same result was obtained by heating the sulphate of phenylhydrazine and several drops of sulphuric acid, or the hydriodate and hydriodic acid, with acet-acetic ether, although the crude pyrazolone formed in these reactions was not as pure as when chlorhydric acid was used. The formation of phenyl-methyl-pyrazolone proceeds, indeed, even in aqueous solution when chlorhydric, hydriodic or sulphuric acid is present. A solution of phenylhydrazine chlorhydrate in 8 parts water with a few drops of chlorhydric acid and acet-acetic ether, in molecular proportions, formed on shaking an emulsion, and the ether soon began to dissolve. After several hours, the time depending on the quantities used, a clear solution was formed, which now contained the chlorhydrate of phenyl-methyl-pyrazolone, as the careful neutralisation of the solution gave that substance in almost the theoretical amount.

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[1] Ann. Chem. (Liebig) **236**, 146.

[2] A. Michael: J. prakt. Chem. [2] **44**, 115.

The experiments on the pyrazolone formation by mineral acids have extended thus far to methyl, ethyl-acet-acetic and acet-succinic ethers, and with these ethers the results obtained were analogous to those just described for acet-acetic ether, with the exception that the chlorhydrate salts of the alkyl-acet-acetic ethers are less soluble in water. For instance, when ethyl-acet-acetic ether is treated with a slightly acid solution of phenyl-hydrazine chlorhydrate, it gradually disappears to make place for a crystalline substance, which melted at 140°–141°, and consisted of the chlorhydrate of phenyl-ethyl-methyl-pyrazolone. By dissolving these crystals in warm water and carefully neutralising with alkalies, the free pyrazolone, melting at 108°, was obtained.

The pyrazolone formation by mineral acids has been used in this research to prove the presence of acet-acetic ether and its homologues, and as only a fraction of a gram is necessary it will be found of use. This reaction may be of service to distinguish between true formyl and ketone-derivatives and those compounds which behave in a similar manner toward free phenylhydrazine, and it will be further studied from this point of view.

The above synthesis of phenyl-methyl-pyrazolone implies the intermediate formation of the "hydrazone," which evidently is unstable in the presence of a mineral acid. To test this view the "hydrazone" was prepared and found to be a solid and not a liquid as described by Knorr. This observation has been recently published by Nef,[1] and I should not mention my results, if they did not differ somewhat from those stated by him. Nef allowed phenylhydrazine to react with acet-acetic ether, added calcium chloride to accelerate the reaction, then extracted the ether solution with dilute sodium hydrate and finally with dilute sulphuric acid. The addition of calcium chloride is unnecessary, as the substances act with great readiness, even under 0°, and give the required amount of water. Extracting with sodium hydrate is also undesirable, as there is no unchanged acet-acetic ether, as Nef assumed, and neutralising the alkaline solution only precipitates phenyl-methyl-pyrazolone. The same remark applies equally to the extraction with dilute sulphuric acid obviously to remove unchanged hydrazine, but by neutralising the extract only pyrazolone is obtained. It will be shown further on that these operations only entail a loss of "hydrazone."

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[1] Ann. Chem. (Liebig) 266, 71.

In my experiments the theoretical quantities of hydrazine, acet-acetic ether and two parts of dry ether were mixed, the solution being cooled in ice, and the mixture allowed to stand for some hours. The water formed in the reaction was removed and the ether solution dried over sodium sulphate. On allowing this solution to evaporate *in vacuo* it gradually solidified to a crystalline mass, which was free from the oil that Nef obtained with his crude product. The product was somewhat yellowish and may be partially purified by extracting with petroleum ether; a pure substance was obtained by dissolving it in a little ether and precipitating by addition of petroleum ether, when it separated as large colorless prisms that began to fall together at about 46° and melted at 50°–51°. According to Nef the solid substance cannot be kept unchanged longer than two days, but the above product underwent no change until after standing several weeks, when it gradually began to turn yellowish, and even after standing for months, it had not turned into an oil, as Nef observed with his substance, but was still almost solid.[1]

In another respect I found a very notable difference between Nef's and my observations, as he claims his product can be heated for a long time at 100° without change, and only passed over into the pyrazolone when heated to 200° in a vacuum. As Knorr showed that the pyrazolone may be prepared by heating his oil to 100°, such a divergence in the stability towards heat would seem to indicate a chemical difference in the solid and liquid "hydrazones." I found on trying the experiment with the solid "hydrazone" that after heating it for a short time at 100° the formation of alcohol began to take place, and that, on sufficiently long heating at that temperature, the liquid turned completely solid and then consisted of phenyl-methyl-pyrazolone.[2]

The "hydrazone" is converted both by mineral acids and by alkalies with the greatest readiness into its pyrazolone. Treated in the cold with dilute chlorhydric or sulphuric acid, it soon went into solution, which then contained the corresponding salt of phenyl-methyl-pyrazolone. The decomposition is about quantitative, and the pyrazolone is obtained almost pure by neutralising the solution carefully with alkalies. A similar result is obtained when the molecular quantity of an alcoholic solution of an alkali is added to the "hydrazone," or when the alkali, in the form of fine powder, is added to a solution of the "hydrazone" in alcohol. The solution turns yellowish, and after several minutes the compound has passed over into the sodium derivative of phenyl-methyl-pyrazolone. This pyrazolone-formation is evidently connected with the decided basic and acid properties of the substance. We have in these reactions good illustrations of that tendency to neutrality which plays so prominent a function in organic chemistry.

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[1] It is not improbable that Nef's product was not perfectly pure, as his carbon estimation is very low.

[2] The solid "hydrazone" was subsequently prepared according to Nef's directions and the product converted by heating at 100° into the pyrazolone. I am at a loss to explain such experimental differences, but it would be certainly of interest if Nef would repeat his experiment.

The above result induced me to re-examine the behavior of aldehydes and ketones towards phenylhydrazine chlorhydrate, and it was found that Fischer's observation[1] regarding the prevention or retarding of hydrazone formation by mineral acids only applies to ketones and not to the aldehydes of monobasic acids. On adding fatty aldehydes to a solution of phenylhydrazine chlorhydrate in water, even when some free acid is present, there is an immediate reaction with the formation of liquid hydrazones, like those Fischer obtained by using the acetate solution. Aromatic aldehydes behave in a similar manner, except that solid hydrazones are formed, that agree in their melting-points with those already described by Fischer.

The retardation is, however, very decided in the case of fatty and aromatic ketones, which act immediately when the acetate mixture is used, but with the chlorhydrate solution gradually only after long standing, although finally the same products are formed. This difference in the behavior of ketones and aldehydes towards phenylhydrazine chlorhydrate is of interest, as it may be used to distinguish between an aldehyde and ketone, and probably also as a means of separating them.

Remarks on J. U. Nef's Paper, "Zur Kenntniss des Acetessigäthers."[2]

A number of the experimental errors to be found in this contribution to our knowledge of the constitution of acet-acetic ether have already been noticed in the preceding pages, and as several other statements made in it seem to support the views peculiar to Nef, the work upon which they are based has been carefully repeated and they, too, have been found inaccurate. It is quite beyond the scope of these remarks to call attention to more than a few of the many mistakes and misconceptions that occur in Nef's paper.

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[1] Ber. d. chem. Ges. **17**, 573.

[2] Ann. Chem. (Liebig) **266**, 52.

In my paper on the constitution of sodium acet-acetic ether I called attention to the strong negative character of its carbonyl-oxygen, and expressed the opinion that the sodium derivative probably consists of a mixture of two compounds,[1] both of which would give the same products with alkyl iodides, but different compounds with alkylene iodides. A number of pages before stating this opinion for the first time[2] I remarked on the different behavior of sodium malonic ether, according to the manner in which it is prepared, and also stated that sodium acet-acetic ether *appeared* to be more difficultly soluble, when prepared in ether solution, or with dry sodium ethylate, than when prepared according to Elion's method. It is perfectly obvious that there was no connection between this experimental observation and the two sodium-acet-acetic ethers which I supposed the known product to consist of.

Nef connects these statements on his own responsibility, then misstates me in assuming the existence of an *insoluble* sodium derivative, and finally asserts that my views on the chemical processes of the acet-acetic ether syntheses must be wrong, because an insoluble derivative does not exist.[3] It is somewhat difficult to imagine a greater confusion of ideas, but, what is still more surprising, it will be shown farther on that Nef has not hesitated to publish as new a good part of the very views he condemns. On page 58 we are informed that alkyl halides should act more readily on the copper, lead and mercury derivatives than on the sodium acet-acetic ether, as the replacing of metal by alkyl takes place more readily with the lead and silver derivatives of phenols and acids than with the sodium compounds. Such assertions are unwarranted, as silver derivatives of acet-acetic ether and phenol are unknown; moreover, only complicated basic lead and mercury compounds of phenol exist, which have never been examined in their behavior towards alkyl halides, and, finally, there are no facts known justifying the assumption that lead in the salts of organic acids is replaced more easily than sodium or potassium. If such considerations have led Nef to believe that the action of alkyl halides on sodium acet-acetic ether only can take place by addition he has obviously reached it through ignorance of the literature on the subject. The hypothesis that the reaction takes place by addition is, however, one of the most essential points in my previous explanations, and Nef has not only borrowed this from my paper without acknowledgment, but the explanation he gave of the formation of dialkyl-acet-acetic ethers is exactly what I had assumed before him.

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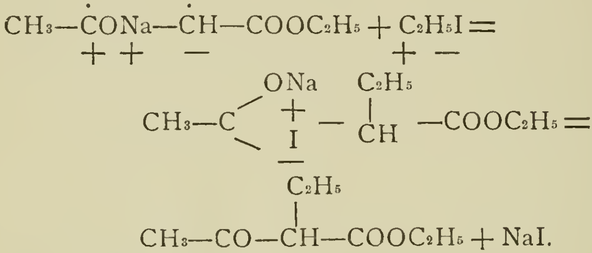
[1] J. prakt. Chem. **37**, 488.

[2] Ibid. 478.

[3] Loc. cit. 56.

In the syntheses of mono-alkyl derivatives our views differ after addition has taken place, and the difference is well explained by the following equations:[1]

I.

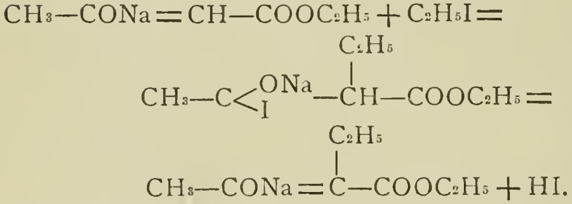


$$CH_3{-}\underset{+\;+}{\dot{C}O}Na{-}\underset{-}{\dot{C}H}{-}COOC_2H_5 + \underset{+\;\;-}{C_2H_5I} =$$

$$CH_3{-}C\begin{matrix}\diagup ONa \\ \overset{+}{\underset{-}{\;}} \\ \diagdown I\end{matrix} - \overset{C_2H_5}{\overset{|}{CH}}{-}COOC_2H_5 =$$

$$CH_3{-}CO{-}\overset{C_2H_5}{\overset{|}{C}}H{-}COOC_2H_5 + NaI.$$

II.



$$CH_3{-}CONa{=}CH{-}COOC_2H_5 + C_2H_5I =$$

$$CH_3{-}C{<}^{ONa}_{I}{-}\overset{C_2H_5}{\overset{|}{C}}H{-}COOC_2H_5 =$$

$$CH_3{-}CONa{=}\overset{C_2H_5}{\overset{|}{C}}{-}COOC_2H_5 + HI.$$

In view of the fact that compounds containing hydroxyl and halogen combined with the same carbon are generally believed to be incapable of existence, as this group decomposes at once into halhydric acid and carbonyl, it is of interest to learn why Nef has made such an entirely improbable suggestion that, not only does ONa and I exist in combination with the same carbon,[2] but that hydriodic acid splits off, instead of sodium iodide, under conditions which are without a precedent among the known instances of the formation of unsaturated acids or their ethers. Nef[3] found that a small quantity of dibenzyl-acet-acetic ether is formed when benzyl chloride acts on sodium acet-acetic ether in alcoholic solution, and claims that this fact can only be explained by assuming that sodium benzyl-acet-acetic ether is a direct product of the reaction, and benzyl chloride acts on a certain number of molecules before the chlorhydric acid has an opportunity to react, although the acid must have just separated from these molecules. The innate improbability of such a conception would be sufficient in itself to condemn it, even though facts were known that appeared to give it support. However, the formation of dibenzyl-acet-acetic ether is very easy to understand, as a stage must exist in this reaction when there is relatively a great deal of benzyl-acet-acetic ether and but little sodium acet-acetic ether present, and our present knowledge of the action of mass, or the division of a base in a mixture of acids, shows that under such conditions some sodium benzyl-acet-acetic ether would be formed and the corresponding amount of acet-acetic ether set free, and the sodium derivative would then react with benzyl chloride. It is hardly necessary to call attention to the fact that the more positive the introduced radicle is, the less di-product should be formed.

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[1] I. is according to the writer and II. is Nef's conception.

[2] How impossible this conception is may be seen from the recent experiments with mandelic nitrile by H. A. Michael and J. Jeanpretre (Ber. d. chem. Ges. 25, 1679), who showed that even the compound $C_6H_5{-}CH{<}^{ONa}_{CN}$ cannot be obtained, as it immediately splits into benzoic aldehyde and sodium cyanide.

[3] Loc. cit. 118.

From pages 63 to 71 Nef considers the constitutions of free acet-acetic and malonic ethers, and a collection of contradictory ideas, supported by inaccurate experimental observations, are stated, such as are, fortunately, seldom seen in a chemical paper. We are informed that phenols act on aromatic amines with the same ease as on aldehydes or ketones, and are referred to Minunni's work,[1] who heated aniline phloroglucinol and calcium chloride for eight hours to 210°, but Nef is evidently unacquainted with the recent literature on phloroglucinol, or he would have known that the conception which best explains the apparent dual nature of this substance is in considering it as a ketone. The formation of a very unstable addition-product of bromine and acet-acet-anilide proves beyond doubt, according to Nef, its constitution as $CH_3—COH=CH—CONHC_6H_5$. Acetic acid unites with bromine to form a stable addition-product, which decomposes at 100° into bromacetic and bromhydric acids. Keptinic ether also unites with bromine to form very unstable bromine addition-product, and must therefore, according to Nef, be an unsaturated compound; but acetic ether forms a comparatively stable addition-product with bromine, and as no chemist, to my knowledge, has ever called acetic acid or its ether unsaturated compounds on account of this property, there is far less reason to attach any importance whatsoever to the supposed addition-products of bromine to acet-acet-anilide[1] and keptinic ether.

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[1] Ber. d. chem. Ges. **21**, 1984.

On page 66 Nef states that methyl- and ethyl-acet-acetic ethers may be converted, in ethereal solution, into their sodium derivatives absolutely without reduction, while diethyl-acet-acetic ether, under similar conditions, is partially reduced. These assertions seemed to me very doubtful, as I had repeatedly prepared the above sodium derivatives and had never obtained the required amount of hydrogen, but, as Nef draws important conclusions regarding a structural difference between ethyl- and diethyl acet-acetic ether from this result, it seemed of sufficient interest to partially repeat his experiments. The ethyl-acet-acetic ether used was a perfectly pure product, obtained by distillation *in vacuo* as already described.

The three experiments were made in the same manner, viz. by distilling off pure and anhydrous ether from sodium. Then the required amount of granulated sodium was added, and the flask, connected with a cooler and a drying tube, allowed to stand 10 hours, when the ethyl-acet-acetic ether was gradually added through a drop-funnel. In all these operations the greatest care was observed to keep the mixture perfectly dry.

I. 1.3 grams sodium under 70 grams ether (slight excess, 1.16 grams being the theoretical quantity) and 8 grams ethyl-acet-acetic ether gave 400 cc. hydrogen at 20° and 735 mm. pressure.

II. 1.2 grams sodium under 50 grams ether and 7 grams ethyl-acet-acetic ether gave 380 cc. hydrogen at 23° and 742 mm.

III. 2.8 grams sodium under 80 grams ether and 16 grams ethyl-acet-acetic ether gave 840 cc. hydrogen at 16° and 748 mm. A slight amount of sodium remained after the reaction had ceased, which gave off hydrogen, when brought into water, corresponding to 0.4 gram sodium, so that the amount of sodium which entered into the reaction was almost that required by theory.

For comparison, ten grams of ethyl-acet-acetic ether will be taken as the unit, and the above stated results will be calculated with reference to that amount:

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[1] Nef calls this compound acet-acetic ether anilide, obviously a misnomer, as there is a connection between the constitutions of these compounds and their chemical names. Acetic ether anilide, to mention an analogous instance, is not used instead of acet-anilide.

Theoretical quantity of H at 0° and 760 mm.	Found at 0° and 760 mm. I.	II.	III.
706.5 cc.	480 cc.	512 cc.	503 cc.

It is very evident from these results that a partial reduction must have taken place, and this fact was easily confirmed by the examination of the product of the reaction. The ethereal solutions were treated with cold water, the alkaline solution immediately extracted with ether, the aqueous residue then acidified and again extracted with ether. On fractionating the last ether-extract a small amount of an acid was obtained, boiling at about 200°, which had the characteristic odor of the higher unsaturated, monobasic acids; and discoloration took place immediately when it was dissolved in carbon disulphide and bromine added, an addition-product being formed without any evolution of bromhydric acid. As the acid also gave the permanganate test, there was no doubt that a reduction takes place in the action of sodium on ethyl-acet-acetic ether. It is not improbable that the ether of an hydroxy acid was first formed, which decomposed on heating to an unsaturated acid, and this was partially saponified by the treatment with alkali, and indeed the regained ethyl-acet-acetic ether was far from being a pure product, as it began to boil under 170°, and between that temperature and 194° over 15 per cent. passed over. I did not examine the lower-boiling portion any further than to notice that it decolorised bromine without formation of bromhydric acid, which indicated the presence of an unsaturated body in it. Nef's conclusion in regard to a structural difference in the constitution of ethyl-acet-acetic ether and the diethyl-derivative is therefore drawn from inaccurate work and has absolutely no foundation.

I find also another incorrect statement in regard to ethyl-acet-acetic ether in Nef's paper, which is that a dilute solution of sodium hydrate extracts that substance from its ethereal solution. Geuther[1] had already shown that ethyl-acet-acetic ether does not dissolve in dilute aqueous alkalies, a statement which Nef therefore puts in doubt. However, Geuther's observation is absolutely correct, as ethyl-acet-acetic ether is only slightly soluble in aqueous alkalies, as it is in water, and ether extracts it from this solution; but if such a solution is allowed to stand, the ether quickly decomposes it into ketone and carbonate. Aqueous alkalies are able to extract ethyl-acet-acetic ether completely from its ethereal solution if shaken with it sufficiently long, but the ether is completely decomposed in this treatment.

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[1] Ann. Chem. (Liebig) **244**, 194.

My experience with the quality of Nef's work on acet-acetic ether had prepared me for experimental errors, but I must confess to astonishment when I came to repeat his experiments regarding the non-action of sodium on dry malonic ether. This ether boils at 195° without decomposition, and there is, therefore, no reason why such a high-boiling liquid should contain even a trace of water or alcohol; moreover, I had repeatedly made sodium malonic ether from a product which had been prepared by repeated fractionation *in vacuo*. According to Nef,[1] malonic ether should not act on sodium, as it is not a carbinol derivative like acet-acetic ether, and he found this to be the case with a product that was allowed to stand for several days with silicium chloride, and then the excess of that reagent driven off by heating the mixture to 130°. This is one of the surest methods of rendering malonic ether impure that the writer is aware off. When pure malonic ether, obtained by fractionating in a vacuum, was mixed with freshly distilled silicium chloride, in such a manner as to avoid the absorption of any moisture from the air, there was no evolution of chlorhydric acid, even if it was allowed to stand for some time, which shows such an ether to be free of water and alcohol; but it was impossible to remove the chloride by heating without the evolution of chlorhydric acid, as it acted on malonic ether, forming a very high-boiling silicium compound. The mixture after heating to 130°, as Nef did in his experiment, still contained a very considerable quantity of unchanged silicium chloride, besides partially decomposed malonic ether, the high-boiling silicium compound, and free chlorhydric acid. Although it was evidently of no importance whether such a mixture was acted on by sodium or not, I tried this experiment and noticed a brisk evolution of hydrogen. It was thought that, perhaps, by heating this mixture of malonic ether and silicium chloride in a vacuum the formation of chlorhydric acid and the high-boiling silicium product might be avoided, and the experiment was repeated, distilling off under 20 mm. pressure and only heating the flask to 50°, but even at that temperature, although the residue was far more free of silicium chloride than when heated to 130° under ordinary pressure, a constant evolution of chlorhydric acid was noticed and some of the high-boiling silicium compound was formed,[1] but not nearly as much as under the conditions of Nef's experiment. This residue was also acted on by sodium in ethereal solution. Pure malonic ether is therefore acted on by sodium, and the conclusion which Nef has drawn from his inaccurate work is evidently wrong.

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[1] Ann. Chem. (Liebig) **266**, 67.

On page 61 the statement is made that the group $COOC_2H_5$ *is less negative than acetyl*, and only six pages farther on we find that if "one considers the ketone constitution of acet-acetic ether and the ordinary structure of malonic ether, then the CH_2 of the last compound must have more developed acid properties than in acet-acetic ether." Although it is interesting to know that by simply considering constitutions more or less acid properties follow, it is somewhat surprising to find that in the present instance the reason depends on $COOC_2H_5$ *being more negative than acetyl!* And again, on page 112, we are told that his considerations must be correct "because $C_2H_5O—CONa{=}CH—COOC_2H_5$ is more negative than $CH_3—CONa{=}CH—COOC_2H_5$." If this, in itself almost unintelligible assertion, be correct, will Nef explain why sodium malonic ether is so unstable that it is decomposed by water, while sodium acet-acetic ether is a stable substance? On page 103 it is stated that considerable tri-acetyl-acetic ether is formed when acetyl chloride acts on copper acet-acetic ether, and on page 110, that chlorcarbonic ether acts on the same salt only to form a mono-substitution product. If Nef's theorising were correct, exactly opposite results should be obtained. On the same page, a reason for the formation of acet-malonic ether only from copper acet-acetic ether is found in the less basic character of copper in comparison to sodium, but referring to pages 102 and 103 we see that the best way of preparing tri-acet-acetic ether is to take copper acet-acetic ether, as the sodium derivative gives mostly the di-acet-acetic ether and comparatively only a very small amount of the tri-acet product!

Finally, I shall call attention to a few more illustrations of the very incomplete knowledge of the literature of the subject on which Nef has based his speculations. On page 69, a perfect understanding of the decomposition of acet-acetic ether by dilute and concentrated alkalies is stated to have been finally gained, although the reasons given are those of Geuther. On page 104, the slight difference between the boiling-points of di-acet-acetic and tri-acet-acetic ether is stated to be due in part to the presence of unsaturated carbons in the first compound, and it is further stated that a double link increases a boiling-point. This is rather difficult to understand, as tri-acet-acetic ether is not a reduction product of the di-acet compound, and, moreover, the broad statement that unsaturated carbons increase the boiling-point of a substance is incorrect, as in some cases with organic ethers and acids there is no appreciable difference, and with other classes of compounds, as is the case with ethyl and propyl alcohol, the boiling-point is lowered by unsaturation. On page 135 the experiment of Friedländer and Weinberg[1] on the formation of ethyl-carbostyrils is explained by assuming an addition as well as substitution when the sodium carbostyril is used, and only substitution when the silver derivative is used. If Nef had been acquainted with the subsequent research of Friedländer and Müller[2] he would have realised that such an explanation does not agree with their results, and if he had referred to my paper, published in 1888, he would have found that the constitution of sodium and silver carbostyril he assumed as new was suggested there, and that Friedländer's results had been explained. The possibility of obtaining carbon-homologues of phloroglucinol by the action of alkyl iodide on the sodium derivative was also predicted in the same paper, before Herzig and Zeisel's work on this subject was published, and explained by addition, as Nef does so much later. In his explanation of the formation of nitriles and isonitriles Nef assumes silver and potassium cyanides to have the constitutions $Ag—N=C$ and $K—N=C$. That these structures are improbable may be shown by a number of reactions, as, for instance, the formation of $CH_3—CO—CN$ from CH_3COCl in AgCN. From his experiments on the brom-alkyl-acet-acetic ethers Nef concludes that the constitution I suggested for tetrinic acid, which Cornelius and Moscheles afterwards confirmed experimentally, is incorrect, since the compound is formed from α-brom-methyl-acet-acetic ether and melts too high to have such a simple constitution. Nef therefore believes it to be a lactide with the structure

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[1] It is my intention to examine the products formed in the action of silicium chloride on malonic ether.

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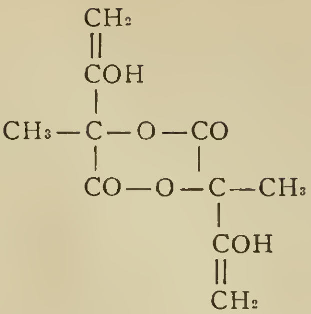
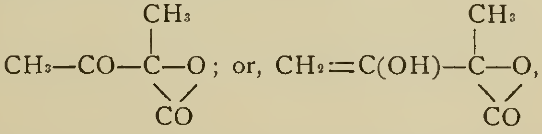
[1] Ber. d. chem. Ges. **18**, 1529.

[2] Ibid. **20**, 2069.



In regard to the melting-point of tetrinic acid I will state that there is no defined relation known at present between this property and the chemical constitution of a substance. How wrong any conclusion drawn from such a property may be is shown in the present instance, as Moscheles and Cornelius[1] have taken the molecular weight of pentinic ether and found it agreed with that required for an ethyl derivative of the constitution I suggested. Nef's lactide constitution must therefore be wrong, and tetrinic acid should therefore have the structure



on account of the strong negative nature of the lactide group. Such a suggestion for the constitution of tetrinic acid shows, what is already evident from all of Nef's speculations, that he never understood the reasons why acet-acetic ether and analogous substances have acid properties, as he himself found that $\mathrm{CH_3{-}CO{-}C}\substack{/\!\!/\,(COC_6H_5)_2 \\ \diagdown\, COOC_2H_5}$ is a neutral body, and the negative influence which acetyl in it is subjected to is incomparably greater than that of a "lactide ring." However, in regard to Nef's work on the action of bromine on acet-acetic ether, its alkyl and the sodium derivatives, it is perfectly evident that the conclusions he has drawn are not substantiated by his work even if it were accurate, but as Hantzsch[2] has already shown that the part relating to ordinary brom-acet-acetic ether cannot be correct and has announced his intention to discuss this part of Nef's work, it is not necessary to enter further on this subject.[1]

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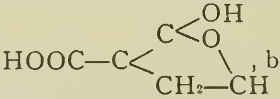
[1] Ber. d. chem. Ges. **22**, 243.

[2] Ibid. **25**, 732.

I shall take this opportunity of replying to several other criticisms of my former research on sodium acet-acetic ether. Elion,[2] misinterpreting my remarks on the solubilities of sodium acet-acetic ether that I prepared by different methods, concludes that I worked with impure sodium acet-acetic ether and, therefore, that it is a matter of doubt whether carb-ethoxyl-acet-acetic ether is really formed from sodium acet-acetic ether. Elion states that my sodium acet-acetic ether was insoluble in ether, but I never made such a statement and simply mentioned that it is pretty (*ziemlich*) insoluble, and Elion's pure product is only soluble in forty parts of ether. If Elion had read my paper more attentively his remarks would have been unwritten, as it is expressly stated that I prepared carb-ethoxyl-acet-acetic ether from sodium acet-acetic ether made in absolute alcoholic solution,[3] and, besides, the large yield obtained made formation of the substance from a partially decomposed sodium acet-acetic ether quite out of the question.

The same remarks apply with greater force to the criticisms of Freund and Gudeman,[4] who ascribed to me a constitution for tetra-methylene-carboxylic acid which I never stated, and then go on to show that their experiments make such a constitution improbable. Tetra-methylene-dicarboxylic acid, according to my views, has the constitution  $\mathrm{HOOC{-}C}\!<\!\begin{matrix}\mathrm{C}\!<\!\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O}\end{smallmatrix}\\ \quad\backslash\\ \mathrm{CH_2{-}CH}\end{matrix}$, but nowhere in my paper have I given a constitution for the monobasic acid, although Freund and Gudeman might have easily inferred it if they had compared the decomposition of the so-called tetra-methylene-dicarboxylic and acetyl-trimethylene-carboxylic acids on heating. As the latter compound is stated to give acetyl-trimethylene ($\mathrm{CH_3{-}CO{-}\dot{C}H{-}CH_2{-}\dot{C}H_2}$), it is evident that tetra-methylene-dicarb-oxylic acid would give $\mathrm{\dot{C}H_2{-}CH_2{-}\dot{C}H{-}\dot{C}OOH}$, and there are at present no results which disprove such a conception of its constitution.

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[1] Nef was also not justified in drawing from Haller and Held's synthesis of citric acid the conclusion that chlor-acet-acetic ether is solely a γ-derivative, as these chemists only claimed that it consisted of a γ- as well as of an α-product, and Hantzsch and Schiffer (Loc. cit. 728) have now shown that it is solely an α-derivative.

[2] Ber. d. chem. Ges. **23**, 3124.

[3] J. prakt. Chem. [2] **37**, 474.

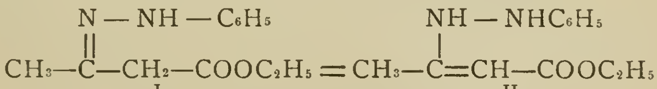
[4] Ber. d. chem. Ges. **21**, 2693.

Theoretical Considerations on the Constitution of Sodium Acet-acetic Ether and Analogous Compounds.

No hypothesis on the constitutions of acet-acetic ether and its sodium derivative can be upheld, unless every known fact concerning these substances is explained by it in a satisfactory manner; and, in the opinion of the writer, this is only possible by considering the free ether as a ketone and the sodium compound as a derivative of a carbinol.

In regard to the ketone constitution of acet-acetic ether the writer[1] has previously shown that the two facts which appeared contradictory are easily brought into accord with it, and it is only necessary to consider two new facts which are found in Nef's paper.

Von Baeyer and Kochendoerfer[2] showed in 1889 that the condensation-product from phloroglucinol and phenylhydrazine is not a hydrazone but a hydrazo-compound, and von Baeyer[3] has recently proven that this is also the case with the succinsuccinic ether derivatives. He explains the reaction by assuming in the first place the formation of an unstable hydrazone, which then passes over into the stable hydrazo-derivative:



$$\underset{\text{I.}}{CH_3-\overset{\overset{\textstyle N-NH-C_6H_5}{\|}}{C}-CH_2-COOC_2H_5} = \underset{\text{II.}}{CH_3-\overset{\overset{\textstyle NH-NHC_6H_5}{|}}{C}=CH-COOC_2H_5}$$

It was evident that the constitution of all the phenylhydrazine derivatives of analogous compounds became an open question, and Nef[4] has since shown that the compound from phenylhydrazine and acet-acetic ether gives results analogous to those obtained

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[1] J. prakt. Chem. **37**, 479-482. [2] Ber. d. chem. Ges. **22**, 2189. [3] Ibid. **24**, 2687-2698.

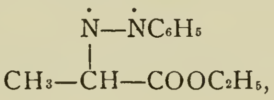
[4] Ann. Chem. (Liebig) **266**, 74. Nef calls the substance acet-acetic ether hydrazide, which is a wrong name, as hydrazides are only formed from hydrazines by replacing hydrogen by acid radicles. The presence of two imide groups in the substance is certainly not proven by the results he obtained by the action of acetyl chloride on it, as the carbon estimation he gives agrees better with that of a mono-acetyl than with his supposed diacetyl product:

Theory for $C_9H_{10}N_2(COCH_3)_2$.	$C_9H_{11}N_2(COCH_3)$.	Found.
67.24	69.4	69.38
6.90	7.3	6.90

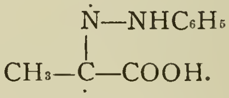
It is not improbable that the compound has a different constitution than that which Nef assigns to it, as a difference of two per cent. in carbon seems too great to be ascribed to error in analysis.

by von Baeyer, and, therefore, is probably not a hydrazone, but a hydrazo-derivative as expressed by II. He concludes from this result that the only experimental fact in favor of the ketone constitution of acet-acetic ether has thereby become invalid.

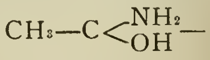
Von Baeyer in his explanation called attention to the mobility of the methylene-hydrogen in acet-acetic ether, and, as the azo group has a strong affinity for hydrogen, it is not in the least surprising that this affinity should cause one of the mobile methylene-hydrogens to pass over to nitrogen; in other words, an intra-molecular reduction takes place. This not only seems probable, but has been proven actually to take place in an analogous reaction, as Japp and Klingemann[1] have shown that the product of the action of diazo-benzene chloride on sodium methyl-acet-acetic ether is not



$$CH_3-\overset{\overset{\dot{N}-\dot{N}C_6H_5}{|}}{C}H-COOC_2H_5,$$



but the hydrazone of pyruvic acid, $CH_3-\overset{\overset{\dot{N}-NHC_6H_5}{|}}{C}-COOH$. This intra-molecular reduction is the result of the same tendency, inasmuch as the azo-compound, which is probably formed at first, takes all the mobile hydrogen available and passes over into a partially reduced group. Fully admitting the possibility of this explanation of von Baeyer, it seems to me that facts are known which indicate a different explanation of this reaction as probable. The formation of hydrazones from aldehydes and ketones and phenylhydrazine is generally believed to be the direct result of a condensation, water being split off; but such a procedure is unlikely, to judge from analogous reactions. The formation of crotonic aldehyde by condensation of aldehyde is preceded by that of aldol;[2] in the synthesis of aldehydes and carbonyl acids with aromatic hydrocarbons by dehydration a similar reaction probably occurs, and in fact has been shown to take place in several instances. With acet-acetic ether there are fortunately results known that leave but little doubt on the subject, as the intermediate products have been isolated. Collie[3] has shown that ammonia and



acet-acetic ether unite to form the compound $CH_3-C<^{NH_2}_{OH}-$

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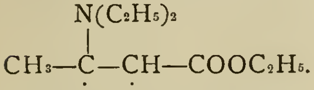
[1] Ann. Chem. (Liebig) **247**, 190.

[2] Michael and Kopp: This Journal **5**, 182.

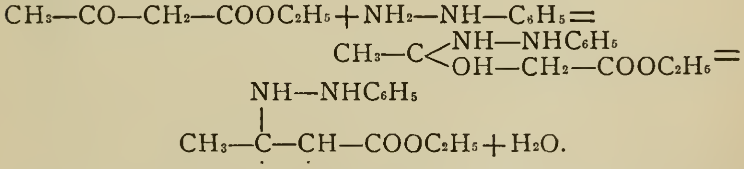
[3] Ann. Chem. (Liebig) **226**, 298.

$CH_2—COOC_2H_5$ by addition, which decomposes, even at 0°, splitting off water and forming $CH_3—\dot{C}NH_2—\dot{C}H—COOC_2H_5$. Still more decisive are Kuckert's results[1] with methyl-amine and di-ethyl-amine, as with the primary base a crystalline addition-product was obtained which gave off water at ordinary temperature, and the secondary base gave a yellowish liquid, probably the addition-product, which decomposes into water and



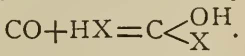
$$\begin{array}{l} \quad N(C_2H_5)_2 \\ \quad | \\ CH_3—\underset{\cdot}{C}—\underset{\cdot}{C}H—COOC_2H_5 \end{array}$$

These experiments indicate that when the ketone-carbonyl of acet-acetic ether acts on bases the primary product of the reaction is an addition. The elimination of water from such an addition-product may take place in two directions, the carbinol-hydroxyl uniting either with a hydrogen joined to nitrogen or with one of the methylene-hydrogens, forming accordingly a hydrazone or hydrazo-compound. Kuckert's results with di-ethyl-amine and von Baeyer's experiments show that it is the methylene-hydrogen that enters into the reaction, and, according to this interpretation, the reaction between phenylhydrazine and acet-acetic ether should be represented as follows:



$$\begin{array}{l} CH_3—CO—CH_2—COOC_2H_5 + NH_2—NH—C_6H_5 = \\ \qquad\qquad\qquad CH_3—C{<}\begin{array}{l} NH—NHC_6H_5 \\ OH—CH_2—COOC_2H_5 \end{array} = \\ \qquad\qquad NH—NHC_6H_5 \\ \qquad\qquad | \\ CH_3—\underset{\cdot}{C}—\underset{\cdot}{C}H—COOC_2H_5 + H_2O. \end{array}$$

It will be seen that the formation of a hydrazo-derivative, and not a hydrazone, is in strict analogy with what is known in the action of bases on acet-acetic ether, and the obtained result tends to confirm rather than disprove the ketone constitution. Our present knowledge of the subject fully justifies the following hypothesis: *If a compound* HX *acts on a substance containing carbonyl* (=CO) *with the elimination of water, such a reaction always takes place in two phases, the first of which consists in the addition of the most reactive hydrogen of* HX *to the carbonyl-oxygen, and of* X *to the carbonyl-carbon:*



$$CO + HX = C{<}\begin{array}{l} OH \\ X \end{array}.$$

Water may then split off in different ways: first, within the molecule, as is the case in the above-described reaction of acet-acetic ether; secondly, several molecules of the addition-product may condense; and thirdly, a reagent with a reactive hydrogen may be present and this hydrogen unite with the hydroxyl of the addition-product. The conditions when one or the other of these three possibilities will happen may be generally foreseen, and I shall return to this subject at another opportunity.

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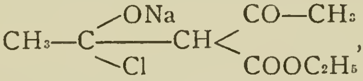
[1] Ber. d. chem. Ges. **18**, 618.

The other point in Nef's paper that needs further consideration is the formation of di-substitution-products in the action of acetyl and benzoyl chlorides on sodium acet-acetic ether, whereas Elion[1] and Nef were unable to obtain a tri-acet-acetic ether by the action of acetyl chloride on sodium di-acet-acetic ether. To explain this Nef adds a second hypothesis to one that I have already shown to be impossible. In the moment when hydrochloric acid splits from  $CH_3{-}C\begin{array}{l}\diagup ONa\\ \diagdown Cl\end{array}{-}CH\Big<\begin{array}{l}CO{-}CH_3\\ COOC_2H_5\end{array}$, the double bond must be more active than afterwards, and therefore, although sodium di-acet-acetic ether does not add acetyl chloride when once formed, it may do so at the moment of formation. This is another of those peculiar results of the double-bond hypothesis which crop out from time to time, only to be forgotten.[2] Our present knowledge of the real nature of the so-called double bond is almost limited to the manifestations of its properties, namely, that it possesses a most remarkable tendency towards saturation, so strong indeed that it often causes the separation of molecules in order to unite with the component parts, and that it is totally different in its nature from the so-called single bond. Double linkage exists only as a name, and there are absolutely no facts known which justify assuming that at the moment of unsaturation the carbons have a greater additive power than afterwards. However, such a difference as Nef claims to exist would be readily explained by my hypothesis.

Di-acet-acetic ether having stronger acid properties than acet-acetic ether, acts therefore on the sodium acet-acetic ether present, forming sodium di-acet-acetic ether. The latter sodium derivative has, at first, the unstable constitution $CH_3\text{—}CO\text{—}\underset{\displaystyle CO\text{—}CH_3}{\underset{|}{CNa}}\text{—}CO_2C_2H_5$, which immediately passes over into the stable form $CH_3\text{—}\dot{C}ONa\text{—}\underset{\displaystyle CO\text{—}CH_3}{\underset{|}{\dot{C}}}\text{—}COOC_2H_5$. But, if a reagent is present, as is acetyl chloride in the case in question, which reacts on sodium when it is joined to carbon, it is easy to understand how a certain amount of tri-acet-acetic ether will be formed by substitution. When once the stable sodium di-acet-acetic ether is formed an addition would take place with difficulty, owing to the, relatively, very negative condition of the unsaturated carbons, and a reaction would, probably, only take place by substitution, in which case the isomeric compound

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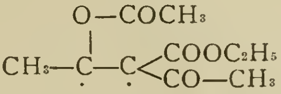
[1] Elion (Recueil trav. chim. 3, 263) seems, however, to leave it a matter of doubt whether a tri-acet-acetic ether is formed or not, and Nef states that he confirmed Elion's results. It is very desirable that Nef should give a more decisive proof that the compound is tri-acet-acetic ether, as his analyses are almost 1 per cent. too low in carbon and hydrogen.

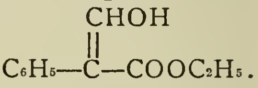
[2] This Journal 5, 194. Demole ascribed a greater volatility to one of the dibromethylenes, for the reason that the carbons in it were not linked.



$$CH_3\text{—}\underset{\cdot}{\overset{\overset{\displaystyle O\text{—}COCH_3}{|}}{C}}\text{—}\underset{\cdot}{C}\!<\!\begin{matrix}COOC_2H_5\\ CO\text{—}CH_3\end{matrix}$$

should be formed.[1] A difference in the behavior of such sodium derivatives at the moment of formation and when they have assumed their stable form, follows directly from my hypothesis, and if Nef's results are correct I can but consider them as strong evidence in its favor.

In regard to the constitution of sodium acet-acetic ether as $CH_3\text{—}\dot{C}ONa\text{—}\dot{C}H\text{—}COOC_2H_5$, such an assumption is absolutely necessary to explain the facts, which the writer has described, on the action of chlorcarbonic ether on it, and analogous constitutions for the alkyl homologues. Among the other facts which make such a constitution probable are the formation of a dihydrofurfuran derivative in the reaction between ethylene bromide and sodium acet-acetic ether, and the difference in the behavior of free acet-succinic ether and its merotropic sodium derivative towards phenylhydrazine.

If, indeed, only the reactions of acet-acetic ether and its sodium derivative were considered the merotropic constitutions of these compounds might be considered as established with a considerable degree of certainty, but the recent researches of Claisen and von Pechmann on analogous compounds again open the subject for discussion. Claisen[1] found that the so-called formyl-camphor has strong acid properties; gives with acetic anhydride an acetyl product, in which acetyl is connected with oxygen, and its sodium derivative does not give a carbon-homologue with ethyl iodide, but a derivative in which ethyl is joined to oxygen. This chemist also showed that formyl-phenyl-acetic ether and acetic anhydride react to give an acetic ether, and concluded from these results that formyl-camphor and other similar formyl compounds in reality do not contain formyl, but are derivatives of unsaturated carbinols. Thus formyl-phenylacetic ether, according to this conception of Claisen, has the constitution  $C_6H_5—\overset{\overset{\text{CHOH}}{\|}}{C}—COOC_2H_5$. These results have been confirmed by von Pechmann,[2] who has examined the behavior of the fatty formyl-acid ethers towards acetic anhydride, and that of their sodium derivatives towards acetyl and benzoyl chlorides, and obtained compounds in which the acid radicles are undoubtedly united with oxygen. Von Pechmann believes that the results of a comparative study of acet-acetic ether and of the analogous formyl-acetic ether will easily prove the constitution of acet-acetic ether, and having only the behavior of the above substances and of their sodium derivatives towards acetic anhydride and acetic chlorides in view, concludes that acet-acetic ether has the ketone-constitution, that its sodium derivative is formed by replacing a methylene-hydrogen by metal, and this form is stable, while formyl-acetic ether has the constitution $HOCH=CH—COOC_2H_5$.

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[1] Elion, indeed, found that acetyl chloride acts on sodium di-acet-acetic ether, but with difficulty. The reaction will be studied to see whether an isomeric product can be isolated.

In reaching this conclusion regarding the ketone-constitution of sodium acet-acetic ether, von Pechmann, accepting Nef's experiments on carb-ethoxyl-acet-acetic ether as correct, has therefore reasoned without considering the one reaction of sodium acet-acetic ether that shows such a constitution to be impossible. If the behavior of sodium acet-acetic ether and its homologues towards chlorcarbonic ether had alone been studied, the results obtained would quite as fully justify the conclusion that sodium in these compounds is joined to oxygen, as the results obtained by von Pechmann on sodium formyl-acetic ether do as regards that compound; especially as the difference in the behavior of acetic anhydride towards acet-acetic and α-formyl-propionic ethers does not, as von Pechmann supposes, justify his conclusion of the latter compound being an alcohol. I[1] have before pointed out that the formation of an acetate by the action of acetyl chloride, or acetic anhydride, on certain ketone and formyl-acids does not imply the existence of a carbinol in such compounds, as it may be the result of an addition to carbonyl and splitting off of chlorhydric or acetic acid. The addition of acetyl chloride and acetic anhydride to aldehydes is a well-known fact, and the ease with which such additions take place appears to increase with the relative negativity of the carbonyl. When the formyl-hydrogen of an aldehyde is replaced by the more positive alkyl to form a ketone, the carbonyl in such a compound is obviously relatively less negative than in the corresponding aldehyde, and, accordingly, there is less tendency on the part of acetyl chloride or acetic anhydride to add to such a carbonyl; but if the negative carboxyl is introduced into a ketone in such a position as to render the ketone-carbonyl sufficiently negative, an addition may take place with the ketone acid thus formed, especially if the carbonyl and carboxyl are in such position that stable acetates may be formed by elimination of chlorhydric or acetic acid. In succinylo-succinic ether the negativity of the ring, loosening of the α-methylene-hydrogen by carb-ethoxyl, and the tendency of reduced benzene derivatives to pass over into a less reduced state, are conditions that cause the formation of an acetate from this ketone-ether; with levulinic acid it is the introduction of carboxyl to carbonyl in the γ-position, and the possibility of the formation of a stable lactone derivative, that induces the acetate formation; whereas levulinic ether does not react with acetic anhydride, because a lactone formation would imply the separation of ethyl and oxygen and, moreover, carbethoxyl is not as negative as carboxyl. But the power of acetic anhydride to unite with aldehydes is not a matter of doubt, and this addition should take place very readily with a compound like formyl-propionic ether, in which the formyl is more negative than in fatty aldehydes. The di-acetyl product which is first formed decomposes under the conditions of the experiment, as do almost all β-derivatives of fatty acids on heating, into an unsaturated compound, and acetic acid or an acetate:

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[1] Chem. Centrbl. **61**, 878.

[2] Ber. d. chem. Ges. **25**, 1040.

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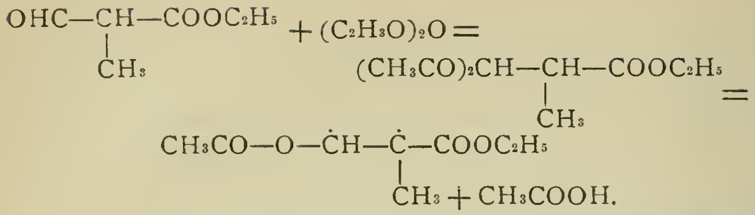
[1] J. prakt. Chem. **37**, 480; **44**, 113.



$$OHC{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOC_2H_5 + (C_2H_3O)_2O = (CH_3CO)_2CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOC_2H_5 = CH_3CO{-}O{-}\dot{C}H{-}\underset{\displaystyle CH_3}{\underset{|}{\dot{C}}}{-}COOC_2H_5 + CH_3COOH.$$

The reason that acet-acetic ether does not behave in an analogous manner is found in the fact that it is a ketone-acid-ether, and if acetyl chloride or acetic anhydride reacted it would be under conditions which the instability of this compound with dehydrating agents renders impossible. In view of this explanation, I do not consider that it follows from this difference in the behavior of acet-acetic, formyl-propionic ether and formyl-camphor, towards acetic anhydride or chloride that the latter compounds are unsaturated carbinols. Far greater difficulty is found in explaining the radical divergence in the results obtained by acetyl chloride on sodium formyl-acetic ether, and the same reagent and ethyl iodide on formyl-camphor, but even these differences will be better understood, if they are regarded in the light of the negative-positive hypothesis.

The assumptions on which this hypothesis are based may be stated as follows: If a relatively negative organic radicle is introduced into any organic compound to take the place of a hydrogen, it renders all the remaining atoms relatively negative in comparison to their previous condition; but the negativisation acts primarily on those atoms in the α-position to the introduced radicle and only secondarily on those in the β-, γ- and other positions, decreasing with the distance between it and these groups.[1] The negativity of the α-carbon is relatively less increased than the positivity of any relatively positive atoms in the α-position is decreased, and the negativity of the α-carbon is relatively more increased than that of any other α-atoms which are more negative than the α-carbon; while the introduction of an organic radicle relatively positive to hydrogen will decrease the negativity of the α-carbon relatively less, than it will increase the positivity of atoms that are positive to this carbon.[2] The extent of these changes stands in a relation to the relative positivity or negativity of the introduced radicle and the influenced atoms, but it is impossible to change the absolute positions of any atoms in the negative-positive series.

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[1] As the atoms of fatty compounds in the γ- and δ-positions appear to be nearer than those in the β, it is evident that mutual influence must be greater in these positions than in the latter.

[2] This hypothesis applies only to relative changes in the positivity or negativity of the atoms of the molecule, and if halogen is present in an unsaturated compound, not only the

The application of this hypothesis explains a number of hitherto imperfectly understood relations of organic compounds; I shall therefore consider several instances as illustrations of its use. In ethane there is, at present, no reason for considering either of its carbons to have a different negativity, but if the relatively negative carboxyl is introduced in the place of a hydrogen, the α-carbon in the compound thus formed will become relatively more negative than the β-carbon, and the affinity of the α-hydrogen for the α-carbon decreased, as compared to the affinity of hydrogen for carbon in ethane. This decrease between the affinity of α-hydrogen for α-carbon will, further, be greater than the decrease between the β-hydrogen and β-carbon, which explains Markownikoff's law on the action of halogens on propionic acid, as also the fact that in condensations it is the α-hydrogen which enters into the reaction.

Ethylene is also a compound in which the carbons may be supposed to have the same negativity, although this does not imply that the negative unsaturated carbons have not a strong affinity for each other, but any negative organic radicle introduced in the place of a hydrogen will render the unsaturated carbons more negative, and therefore decrease their affinity for negative, but increase it for positive atoms; while the introduction of a positive radicle will have exactly the reverse effect. When a negative radicle, as carboxyl, is introduced into ethylene the unsaturated carbons are no longer of equal negativity, but the α-carbon is relatively more negative than the β-carbon, and, for that reason, when an addition takes place to these unsaturated carbons, the positive part of the additive compound will unite with the relatively more negative α-carbon, and the negative part with the less negative β-carbon.

Introducing a positive radicle like methyl, in the place of a hydrogen, forms propylene, and in this compound the α-unsatur-

condition of the unsaturated carbons but also the specific affinity of the halogen has to be taken into account. I wish further to point out that in radicles like methylene the unsaturated carbons have a strong affinity for each other, and any change which makes both these carbons more negative will decrease their affinity for each other, although it may put them in a state of positive-negative contrast. If it were possible absolutely to increase the positivity of one of the carbons and decrease that of the other it is probable that their affinity for each other would be greater than in ethane, but such changes are impossible in organic transformations.

ated carbon has therefore become relatively positive to the β-carbon. When an addition of a halhydric acid to the unsaturated carbons of propylene takes place the negative halogen will unite with the relatively positive α-carbon, and the positive hydrogen with the relatively negative β-carbon. We have here a rational explanation of the empirical laws of Markownikoff and Erlenmeyer on the addition of halhydric acids to unsaturated fatty hydrocarbons and αβ-fatty acids; but, as I have previously shown,[1] the application of the negative-positive hypothesis to the question of addition not only explains it, but has a much more extended application than these empirical rules.

When carboxyl replaces a hydrogen of ethylene, we have seen that the α-carbon is more influenced by this negative radicle than the β-carbon, and, therefore, the α-unsaturated carbon of acrylic acid should have a greater affinity for the positive hydrogen of bromhydric acid than either of the carbons of ethylene; while the β-carbon of acrylic acid, being relatively negative to the carbons of ethylene, will have less affinity for the bromine, but, as the α-carbon has increased in its negativity in greater proportion than the β-carbon, it follows that acrylic acid should add bromhydric acid more easily than does ethylene. The introduction of a carboxyl into the place of an α-hydrogen of acrylic acid does not necessarily lead to an analogous result, as the α- and β-unsaturated carbons of acrylic acid are already in a relatively positive and negative state and therefore, according to the above hypothesis, will be changed to a different extent. The α-carbon of acrylic acid being relatively negative will undergo a less relative negativisation by the introduced carboxyl than the comparatively positive β-carbon; in fact there would be the same relative changes, although in less degree, as α-carbon and α-hydrogen undergo when a negative radicle is introduced. In $\underset{+}{\dot{C}H_2}—\underset{-}{\dot{C}}=(COOH)_2$ the unsaturated α-carbon should have a greater affinity for the hydrogen of bromhydric acid than has the α-carbon, and the β-carbon a less affinity for bromine than has the β-carbon, of acrylic acid, but it does not follow that the acid $CH_2—C=(COOH)_2$ would take up hydrobromic acid more easily than acrylic acid, because the affinity of the β-carbon for bromine may have been diminished to a relatively greater extent than the affinity of α-carbon for hydrogen increased. Whether the introduction of a second negative radicle may, therefore, increase or diminish the additive power probably depends on the relative negativity of the introduced radicle, the more negative it is the more likely is a diminishing of the comparative additive power.

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[1] J. prakt. Chem. **37**, 525; **40**, 171.

It has been shown that propylene should have a greater additive power for hydrobromic acid than ethylene, and the question arises, whether the introduction of a positive radicle like methyl in the α-position will cause a relative increase or diminution in this additive power? The effect of introducing an α-methyl into propylene on the unsaturated carbons, which were already in a relatively positive-negative state, would cause the same changes as if the β-carbon were a more negative atom than the α-carbon; in other words, the relative positivity of the α-carbon would undergo a comparatively greater increase than the relative negativity of the β-carbon would suffer a decrease. It follows that the α-carbon would have a relatively greater increase in its affinity for bromine than the decrease of the β-carbon for hydrogen, and therefore that isobutylene should have a greater additive power for hydrobromic acid than propylene.

It is of interest to see how far experimental results agree with the conclusions obtained by the application of the "positive-negative" hypothesis in regard to the addition of substances to unsaturated compounds, and I shall therefore mention a few illustrations. Ethylene does not unite with chlorhydric acid even when heated with it; propylene very slowly in the cold but more readily at 100°,[1] but isobutylene unites with chlorhydric acid in the cold,[2] and when the acid is passed through an alcoholic solution of acrylic acid it unites and etherises it to form β-chlorpropionic ether.[3] Further, ethyl-vinyl is unacted on by chlorhydric acid under the same conditions as those under which isobutylene readily unites with it to form tertiary butyl-chloride;[4] and unsymmetrical ethyl-methyl-ethylene unites with sulphuric acid under conditions that leave trimethyl-ethylene unchanged.

Before applying the positive-negative hypothesis to the reactions of acet-acetic ether and analogous substances, it will be well to call attention to the necessity, in such speculations, of comparing similar radicles, as, if they are unlike in their structure, it is not permissible to infer from their constituent atoms that the unsaturated carbon of a radicle is necessarily relatively more positive or negative than that of the other radicle. It has already been shown that Nef at times considers $COOC_2H_5$ as positive to CH_3CO and again negative, although the properties of compounds containing the group $COOC_2H_5$, show, beyond doubt, that it behaves as a less negative radicle. This paradoxical conclusion may be understood when one considers that the relative negativity of the unsaturated carbons of $COOC_2H_5$ and CH_3—CO depends, not only on the negative-positive relations of the constituent atoms, but also on their distances from these atoms, and it is possible that the ethyl of $COOC_2H_5$, although united with oxygen, may have a greater positive influence than methyl, owing to its being less distant.

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[1] Berthelot: Compt. rend. **44**, 1350.

[2] Ann. chim. phys. [5] **28**, 549.

[3] Ann. Chem. (Liebig) **163**, 95.

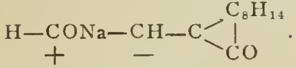
[4] Le Bel: Compt. rend. **85**, 852.

The application of these speculations to the problem of the reactions of sodium acet-acetic ether and analogous substances, will be more easily followed by arranging the formulas of the compounds thus:

I. $H_5C_2O-\underset{+}{CONa}-\underset{-}{CH}-COOC_2H_5.$

II. $H_3C-\underset{+}{CONa}-\underset{-}{CH}-COOC_2H_5.$

III. $H-\underset{+}{CONa}-\underset{-}{CH}-COOC_2H_5.$

IV. 

$H-\underset{+}{CONa}-\underset{-}{CH}-C\!<\!\begin{array}{l}C_8H_{14}\\ |\\ CO\end{array}.$

V. $H-\underset{+}{CONa}-\underset{-}{CH}-COOC_2H_5.$

VI. $H_5C_2OOC-\underset{+}{CONa}-\underset{-}{CH}-COOC_2H_5.$

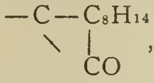
VII. $CH_3-\underset{+}{CONa}-\underset{-}{CH}-COOC_2H_5.$

VIII. $CH_3-\underset{+}{CONa}-\underset{-}{C}=(COOC_2H_5)_2.$

In sodium acet-acetic ether (II) the relations between the positivity and negativity of the unsaturated carbons are such that they are able to cause the addition of a substance like ethyl iodide, whose additive components differ considerably in their positivity and negativity, and also of a compound like acetyl chloride, both of whose parts are negative, but not strongly united. Chlorcarbonic ether may be classed between such compounds as ethyl iodide and acetyl chloride, as its halogen is considerably more firmly united to carbon than chlorine is in acetyl chloride. It is possible that, with such a compound, the additive power of the unsaturated carbons in sodium acet-acetic ether, and the tendency of the halogen to unite directly with sodium are approximating an equilibrium, in which case a part of the reaction should take place by substitution and, at the same time, a certain proportion of the reagent should unite by addition to the unsaturated carbons. In the case of sodium acet-acetic ether it would seem as if addition predominated, since comparatively little acet-malonic ether is formed.

Sodium malonic ether (I) may be considered as formed from sodium acet-acetic ether by replacing methyl by the relatively more positive ethoxyl, and we have seen that such an interchange increases the affinity of the unsaturated carbons for negative atoms or radicles, and also increases the relative difference of the positivity and negativity of these carbons. If acetyl chloride acts on sodium acet-acetic ether by addition, it will be added still more readily to sodium malonic ether, but the relative increase in the affinities of the unsaturated carbons is also sufficient to cause the separation of the more strongly joined chlorine and carb-ethoxyl of chlorcarbonic ether, and this action is therefore solely the result of an addition.

Sodium formyl-acetic ether (III) stands in the relation to sodium acet-acetic ether that a hydrogen is replaced by the more positive methyl. In this compound, therefore, the unsaturated carbons are comparatively more negative than those of sodium-acet-acetic ether, and therefore have less tendency to cause the addition of a reagent like acetyl chloride, whose additive components are both negative; and there is also a relative decrease of the additive power of the unsaturated carbons for a reagent like ethyl iodide, whose components are positive and negative, in comparison with those of sodium acet-acetic ether. Such a change favors substitution with acetyl chloride, and hence von Pechmann obtained an acetate in this reaction.[1]

Finally, to complete this series, comparing sodium formyl-camphor (IV) with sodium formyl-acetic ether, we have the replacement of the negative carb-ethoxyl in the latter compound by the more negative radicle  $\begin{array}{c}-\mathrm{C}-\mathrm{C_8H_{14}}\\ \diagdown\quad|\quad\\ \mathrm{CO}\end{array}$, and its unsaturated carbons have therefore a still less affinity for chlorine and acetyl than those of sodium formyl-acetic ether. This reaction, therefore, takes place, as Claisen has shown, by substitution. The relative positivity and negativity of the unsaturated carbons also may have been decreased, as both the α-hydrogens are replaced by negative radicles, and in this compound a stage is reached where even ethyl iodide no longer acts by addition, but only by substitution.

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[1] It is probable that methyl iodide would act at least partly by addition, and this experiment will be made. Acetyl chloride acts quite readily by substitution even if the sodium is united with a negative radicle, as is seen by the formation of acetic anhydride from it and sodium acetate.

In the second column we have the constitutions of sodium formyl-acetic and sodium oxal-acetic ethers, and it is evident that the unsaturated carbons in the latter compound are relatively more negative. We may therefore expect that acetyl chloride would act by substitution, although there have been no experiments in this direction. Methyl iodide acts by addition, but with difficulty and only a poor yield is obtained. In the same column sodium acet-malonic and sodium acet-acetic ether have been placed together for comparison. The former compound may be considered as formed from the latter by replacing a hydrogen by the negative carb-ethoxyl, which renders its unsaturated carbons relatively considerably more negative and may decrease their relative positivity and negativity. This substance has such a negative character, and the affinity of carbon for carbon is so loosened thereby, that neither with acetyl chloride nor ethyl iodide have derivatives of it as yet been obtained.

It appears to the writer that, however imperfect these speculations on sodium acet-acetic ether and analogous compounds may be, they afford an indication why such apparently similar products behave so differently, and at least merit attention as pointing to a method of investigating this most intricate problem. Claisen and von Pechmann have pointed out that the constitutions they assign to formyl-camphor and formyl-acetic ether would invalidate the generalisation of Erlenmeyer's law on the non-stability of vinyl alcohol and derivatives of it, and this assumption, in connection with the results described in this paper on sodium acet-acetic ether, make the constitutions they assign to their compounds appear improbable.[1]

BONCHURCH, ISLE OF WIGHT, *May*, 1892.

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[1] Since the above paper was handed in for publication, two communications, touching in part on the same subject, have been published by Claisen (Ber. d. chem. Ges. **25**, 1760, 1776), in which he has called attention to some of the errors of experimentation and reasoning to be found in Nef's paper on acet-acetic ether, and has confirmed my previous view on the constitution of carb-ethoxyl-acet-acetic ether.

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON AROMATIC SILICIC ETHERS.

By H. N. Stokes.

In a paper on the action of phosphorus oxychloride on ethyl silicates and chlorsilicates[1] (chlorhydrines), I have shown that this reagent converts ethyl orthosilicate completely into ethyl chloride and silico-pyrophosphoryl chloride, $SiP_2O_6Cl_2$, and that the ethyl orthochlorsilicates yield under the same conditions these bodies and silicon tetrachloride, the amount of the latter being proportional to the amount of chlorine in the silicon compound used, the trichlorsilicate yielding most, while tetra-ethyl silicate gives none.

$$4SiCl_3(OC_2H_5) + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4C_2H_5Cl.$$
$$Si(OC_2H_5)_4 + 2POCl_3 = SiP_2O_6Cl_2 + 4C_2H_5Cl.$$

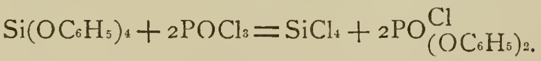
It was not thought worth while to repeat these experiments with other silicic ethers of the aliphatic series, as similar results were to be expected.

In view of the different properties in general of aromatic bodies, the action of phosphorus oxychloride on silicates of this class could not be foreseen. I have therefore treated *phenyl orthosilicate*[2] with phosphorus oxychloride, and have obtained results which show in a striking manner the difference between aliphatic and aromatic silicates.

The proportion selected was that required by the equations—

$$Si(OC_6H_5)_4 + 2POCl_3 = SiP_2O_6Cl_2 + 4C_6H_5Cl,$$

or



$$Si(OC_6H_5)_4 + 2POCl_3 = SiCl_4 + 2PO\overset{Cl}{\underset{(OC_6H_5)_2}{}}.$$

The mixture, after being heated 3–4 hours at 170°–180° (the temperature at which the ethyl silicates react with phosphorus oxychloride), was distilled. No indication whatever of a reaction could be discovered, the oxychloride being recovered unchanged, and proved to be absolutely free from silicon compounds. After being heated 16 hours at 240°, the liquid was somewhat discolored, but perfectly clear. On fractioning, it was easily separated into silicon tetrachloride (b. p. 59°), phosphorus oxychloride (b. p.

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[1] This Journal **13**, 244; Ber. d. chem. Ges. **24**, 933.

[2] Hertkorn: Ber. d. chem. Ges. **18**, 1679.

109°), and chloride of phenyl-phosphoric acid, $POCl_2(OC_6H_5)$ (b. p. 240°–243°), with a residue consisting of chloride of di-phenylphosphoric acid, $POCl(OC_6H_5)_2$ and phenyl phosphate.

The fraction of b. p. 59° gave—

	Calculated for $SiCl_4$.	Found.
Si	16.47	16.24

The amount of tetrachloride was approximately equivalent to the quantity of phenyl silicate used, while the higher-boiling portions and the residue were found to be practically free from silicon, thus proving the conversion into tetrachloride to be complete. Not a trace of chlorbenzene or silico-phosphoryl chloride was formed.

It will be noticed that while the ether is completely converted into chloride, the reaction does not proceed strictly according to the second of the above equations, but that a mixture of phenyl phosphate with the chlorides of the two phenyl-phosphoric acids results, some of the oxychloride remaining unchanged.

By means of this reaction and that described previously,[1] it is easy to convert aromatic or aliphatic orthosilicates into silicon tetrachloride. The aromatic ethers, heated with phosphorus oxychloride, give the tetrachloride directly; the aliphatic ethers yield silico-pyrophosphoryl chloride, which is readily converted into silicon tetrachloride by heating with phosphorus pentachloride[2] at 100°. Phosphorus pentachloride, used directly, effects the transformation only with great difficulty. Friedel and Crafts[3] have shown that the pentachloride readily converts ethyl orthosilicate into ethyl monochlorsilicate, $SiCl(OC_2H_5)_3$. I have found that this reaction cannot readily be pushed further than the trichlorsilicate, $SiCl_3(OC_2H_5)$. This body holds the ethoxyl very firmly, and even after heating many hours at 140° with pentachloride, but little silicon tetrachloride is formed. If heated much higher, the pentachloride liberates chlorine, causing total destruction of the ether. Acetyl and benzoyl chlorides effect complete conversion into tetrachloride, but only when used in large excess and on heating at over 200° for a very long time.

I am studying the action of various metallic haloid salts, especially those of aluminium, on silicic ethers, and have observed a similar difference; aluminium chloride, for example, readily converting the aromatic ethers into silicon tetrachloride, while its action on aliphatic ethers is entirely different and much more complex, the products depending on the nature of the ether taken and the proportional amount of aluminium chloride used. The results will be described in a separate paper.

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[1] This Journal **13**, 248.

[2] Ibid. **13**, 247.

[3] Ann. chim. phys. [4] **9**, 14.

U. S. GEOLOGICAL SURVEY, WASHINGTON, *July*, 1892.

NOTE ON BENZYL SILICATE.

BY H. N. STOKES.

As is known, both ethyl alcohol and phenol, if perfectly anhydrous, produce with silicon tetrachloride the corresponding *ortho*-silicates in nearly theoretical amount, the chief difference being that while ethyl alcohol acts violently, with reduction of temperature,[1] phenol requires prolonged boiling for complete conversion into the ether, the evolution of hydrochloric acid being scarely noticeable at ordinary temperature.[2]

Anhydrous *benzyl* alcohol, as was to be presumed, behaves towards silicon tetrachloride as an aliphatic alcohol, not as a phenol, violent action with fall of temperature occurring. The reaction is not smooth, however, as in the case of ethyl alcohol. A large amount, perhaps one-fourth, is converted into *benzyl chloride*, either by direct action of the hydrochloric acid evolved, or indirectly by action of the latter on the benzyl silicate. As a result, if the calculated amount of alcohol be taken, much remains unchanged, and the tetrachloride is largely converted into polysilicates. On distilling the mixture under atmospheric pressure, some benzyl silicate passes over, but this is completely broken up by one or two redistillations. The products of decomposition consist of water, toluene, stilbene, anthracene and high-boiling products of undetermined nature. As no particular interest attaches to benzyl silicate, no further attempt was made to isolate it.

This formation of benzyl chloride recalls the action of benzyl alcohol on boron trichloride,[3] when the chief product is benzyl chloride.

U. S. GEOLOGICAL SURVEY, WASHINGTON, *July*, 1892.

[1] Ebelmen: Ann. Chem. (Liebig) **57**, 334.

[2] Hertkorn: Ber. d. chem. Ges. **18**, 1679.

[3] Councler: J. prakt. Chem. [2] **18**, 396.

RESEARCHES ON THE SUGAR OF THE *AGAVE AMERICANA.*

By Gustave Michaud and José Fidel Tristan.

With the juice extracted from the stalk of the *Agave Americana,* the Mexicans make an intoxicating beverage called *pulque.* This plant is extensively grown in Mexico for this purpose; its culture is lucrative, as it grows in barren as well as in fertile grounds and requires but little care. These facts suggested to us the thought that the plant might perhaps be used industrially as a source of sugar, and this idea led us to examine the nature of the sugar contained in the Agave.

We could not obtain, at first, the stalks we wanted, and began our work with the leaves. These are thick and full of a juice that exhales a nauseous smell. We cut the leaves into small pieces and squeezed them dry with a screw-press. The juice was mixed with two volumes of 90-per cent. alcohol and left during 24 hours in a cool place; then it was filtered. The alcohol was distilled off and the aqueous residue mixed with basic acetate of lead. Care was taken to reduce to a minimum the excess of the latter reagent. After filtration, the lead was removed by a current of sulphuretted hydrogen and the filtered liquid was submitted to polarimetric examination. In spite of its sugar-like flavor it was inactive.

It reduced Fehling's solution; 0.45 cc. of the liquid being necessary to reduce 10 cc. of the reagent. According to this experiment, and admitting that the reducing power of the sugar contained in the Agave was equal to that of glucose, the solution should have contained 11.11 per cent. of sugar. But the following determination gave a result altogether different: 20 cc. of the liquid were evaporated at a low pressure to a sirupy consistency and left during a few hours in a flat saucer, upon a drying oven, in a lukewarm place. Little by little there occurred a change in the consistency and in the color, which became lighter from the margin to the centre. The solid mass was then examined with the microscope and was found to be made up of small crystals. When these were thoroughly dried their weight was 3.716 grams; this showed a concentration of 18.58 per cent.

Then 100 cc. of liquid were mixed with 10 cc. of hydrochloric acid, heated a little while at 100° C., and cooled. Submitted to polarimetric observation it gave a rotation of —5.92°. Its richness in sugar was determined with Fehling's solution. After the necessary reductions for dilution, it was found that it took 0.27 cc. of liquid to decolorise 10 cc. of Fehling's solution. These numbers showed a concentration 18.52 per cent., which was only a little inferior to that which could be calculated (19.55) from the concentration of the liquid previous to its inversion and such as had been shown by the evaporation of 20 cc.

From these experiments it might be inferred that the Agave contained an inactive sugar whose reducing power was about five-eighths of that of glucose, and which could be inverted and transformed into another or into various others whose rotatory power or the algebraic sum of whose rotatory powers was = —14.53°.

It might also have been supposed that the Agave contained not only one class of sugar but a mixture of sugars, and that the inactivity of the sugared juice was the result of an exact compensation. The following experiments showed the value of this hypothesis:

Various stalks were squeezed less than an hour after being cut. The juice was submitted to the same treatment as before, but after elimination of the lead it was concentrated, under low pressure, to a sirupy consistency; then it was treated with some animal charcoal and examined with the polarimeter. It showed a rotation of +0.73°. 10 cc. were evaporated to dryness. They contained 7.103 grams of sugar. These numbers showed a rotatory power of $[\alpha]_y = 0.51$. It was thought that this optical action of the syrup might not belong to the sugar that formed the bulk of it, but to an impurity such as glucose, and in order to verify this hypothesis, the sugar was purified by three crystallisations made as before, the crystalline powder being each time compressed between sheets of filter-paper. Then 39.242 grams of dry crystals were dissolved in 100 cc. of water and the solution submitted to polarimetric observation. It was inactive.

Having thus acquired the certitude of having isolated an inactive sugar in a state of purity, we proceeded to the following experiments in order to determine its most important characteristics.

Two combustions of the crystals were made; they gave the following results:

	Calculated for $C_{12}H_{22}O_{11}$.	Found. I.	II.
C	42.10	41.82	41.79
H	6.43	6.50	6.54

An aqueous solution of the Agave sugar was mixed with lime. After filtration it was verified that the liquid was precipitated by heat or by addition of alcohol. Submitted to the action of a current of carbonic acid it regenerated an inactive sugar, probably identical with the Agave sugar.

The products of oxidation of the sugar were examined for the purpose of determining the presence of mucic acid. 2 grams of sugar were dissolved in 3 cc. of water and mixed with 12 cc. of nitric acid. After it had ceased emitting nitrous vapors, the volume of the liquid was reduced by evaporation to 3 cc., then it was mixed with 15 cc. of water. The liquid remained perfectly transparent, thus showing, by this negative reaction, the absence of mucic acid among the products of oxidation.

Two solutions of pure sugar were used to determine the rotatory power of the products of inversion. After being mixed with one-tenth of hydrochloric acid they were heated at 100°, cooled and examined with the polarimeter. The following figures express the result of this determination. C = concentration = quantity of active substance dissolved in one cubic centimeter of solution, the determination being made with Fehling's solution.

	C	a	λ	$[a]_{v}$
I.	0.3920	—12.41	2.2	—14.390
II.	0.5035	—16.28	2.2	—14.470

The results of the preceding investigations may be stated in the following conclusions:

The *Agave Americana* contains a sugar of the formula $C_{12}H_{22}O_{11}$. This sugar differs from all other sugars of the same group, except synanthrose, by its inactivity. It differs from synanthrose by its power of crystallising, by its action in Fehling's solution, and by the rotatory power of the products of its inversion.

We propose for this sugar the name of *Agavose.*

SAN JOSÉ, COSTA RICA.

REVIEWS.

Scientific Correspondence of Joseph Priestley. Ninety-seven letters addressed to Josiah Wedgwood, Sir Joseph Banks, Capt. James Keir, James Watt, Dr. William Withering, Dr. Benjamin Rush, and others. Together with an appendix—I. The Likeness of Priestley in Oil, Ink, Marble, and Metal. II. The Lunar Society of Birmingham. III. The Inventory of Priestley's Laboratory in 1791. Edited, with copious biographical, bibliographical and explanatory notes, by H. Carrington Bolton. New York: Privately printed, 1892. viii + 240 pp. 8vo.

Dr. Bolton deserves the thanks of chemists and others for this labor of love. The letters here presented to the public for the first time will be read with interest, and will help the present generation better to understand that remarkable man, Joseph Priestley, who seems not to have been well understood in his lifetime—even by himself. The editor of the letters remarks: "The ideal sketch of Priestley as an investigator in science is, we think, yet to be written; we do not attempt in the following pages to supply this want, but rather to contribute material for some future historian to use in such a work. The advantages afforded by letters to obtain insight into the very thoughts of their writer, and to illustrate his character, are acknowledged by all, and with this in view we have collected and annotated the correspondence which here follows." Among the most interesting of the letters are those written to Josiah Wedgwood. In regard to these Dr. Bolton says; "The previous references to these letters by no means detract from the interest attached to their present publication; they cover a period of thirteen years (1780–1792) and compose the whole of the extant correspondence between the chemist and the potter. They treat almost exclusively of scientific matters, and are written in the confiding spirit which characterised the friendly intercourse of the men of science. Priestley often sat down to write his friend while flushed with delight at the completion of a successful experiment, sometimes even before his crucibles had cooled; and feeling assured that his communications would be received by a sympathising reader, he wrote his first impressions, his hopes and his plans with a naturalness and self-portrayal pleasant to behold."

A Manual of Chemistry, Inorganic and Organic, with an Introduction to the Study of Chemistry. By Arthur P. Luff, M. D., etc. Philadelphia: Lea Brothers & Co., 1892.

Here it is again. Possibly in the millennium there will be medical students able to comprehend the atomic theory and all that that implies before they have learned anything about chemistry. Certainly the medical students of the present cannot do it. And why should they try? Hear this. "The formulæ of these acid radicals and their quantivalences, together with the symbols of the elements and their atomicities, must be thoroughly committed to memory; the student will then be able easily to construct formulæ, the representation of chemical reactions by means of equations is but another step forward." The student will not only be able to construct formulæ, but he will probably go on constructing formulæ under the impression that he is learning chemistry. The writer of this notice sometimes thinks, and the intervals between the thoughts are getting shorter, that if the use of formulæ were given up entirely in elementary instruction better results would be obtained. If the book under consideration is to be used by medical students, and that is what the author hopes, the first seventy pages should be omitted, and a simple, comprehensible introduction supplied by the teacher. But, even as regards the rest of the book, all that can be said is that it is "pretty good," and as, in the world to come, there is (it is stated) no room for "pretty good" people, so there is no room in this world for "pretty good" text-books on chemistry. I. R.

THE PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS. By IRA REMSEN, Professor of Chemistry in the Johns Hopkins University. Fourth edition, thoroughly revised. Philadelphia: Lea Brothers & Co., 1892.

"In preparing this new edition I have been tempted to change the book fundamentally and give it a character more in keeping with the recent tendencies of work in the field of Physical or General Chemistry. But, taking everything into consideration, I have concluded to resist the temptation, and remain true to the original title and character of the book. Accordingly, it is essentially what it has been—a brief treatise on those facts and speculations that have to deal especially with the problem of the constitution of chemical compounds. My object has been, and is, to help students to get clear ideas in regard to the foundations of chemistry. That the treatment has been regarded with favor is shown by the fact that four editions of the book have been demanded in a comparatively short time; and, further, by the fact that, since the appearance of the last American edition, it has been translated into German and into Italian. I believe that all changes called for by the advance of the science have been made, and that this edition will be found abreast of the times. The chief addition is a short chapter on Solutions."—*The Preface.*

VOL. XIV. [DECEMBER, 1892.] No. 8.

AMERICAN

CHEMICAL JOURNAL.

Contribution from the Chemical Laboratory of Clark University, Worcester, Mass.

THE ADDITION-PRODUCTS OF BENZO- AND OF TOLUQUINONE.

BY T. H. CLARK.[1]

The presence of two pairs of doubly-bound carbon atoms in benzoquinone has been made highly probable by the work of Nef,[2] who obtained a dibromide and a tetrabromide. The following experiments, which have been carried out under the direction of Dr. Nef, are a continuation of the study of the addition-products formed by quinones. Up to the present time five addition-products of quinone have been obtained, namely a di- and a tetrabromide, a di- and a tetrachloride and a dichloride-dibromide. These five compounds are all strictly analogous and quite stable —the chlorine derivatives most so.

The dichloride and dibromide have a faint quinone-like odor, are light-colored, moderately soluble in organic solvents, and soluble without change in fuming nitric acid. The other three are colorless, inodorous, and very sparingly soluble in organic solvents; they dissolve with difficulty and without change in warm fuming nitric acid. All five products are instantly decomposed by dilute sodic hydroxide; they all split off halogen hydride (one or two molecules) on warming the alcoholic solutions, and go over into one, or two isomeric, halogen-substituted benzoquinones. Treated with zinc and acetic acid, all the halogen atoms are eliminated and hydroquinone is obtained from all.

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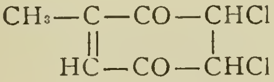
[1] Accepted as a thesis for the degree of Doctor of Philosophy at Clark University, June, 1892.

[2] This Journal **12**, 483; **13**, 423.

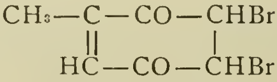
The decomposition-products of quinone dichloride-dibromide formed by boiling it in alcoholic solution are meta- and parachlorbromquinone; and this proves, beyond a doubt, that the addition of halogen, as well as the splitting off of halogen hydride from the resulting addition-products, takes place exclusively in the ortho position, as has already been elucidated in a previous paper.[1]

Toluquinone forms a dibromide and a dichloride, but all attempts to obtain a tetra-halogen addition-product were fruitless. The products obtained closely resemble the corresponding benzoquinone bodies. Reduced with zinc and acetic acid, the halogen atoms are taken out and hydrotoluquinone results. On boiling an alcoholic solution of toluquinone dichloride it loses one molecule of hydrochloric acid, and meta- and parachlortoluquinone are formed. This proves that the addition of the halogen atoms has taken place, not on the propylene side of the toluquinone molecule, as was expected, but on the ethylene side; *i.e.* the addition-products must have the constitution represented by the formulæ:



$$\begin{array}{ccccccc} CH_3 & - & C & - & CO & - & CHCl \\ & & \| & & & & | \\ & & HC & - & CO & - & CHCl \end{array}$$

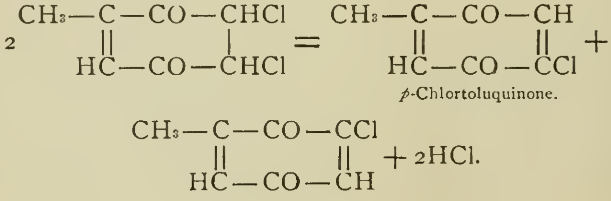
Toluquinone dichloride.



$$\begin{array}{ccccccc} CH_3 & - & C & - & CO & - & CHBr \\ & & \| & & & & | \\ & & HC & - & CO & - & CHBr \end{array}$$

Toluquinone dibromide.

It is evident then that the dichloride, for instance, can lose one molecule of hydrochloric acid and give a mixture of meta- and parachlortoluquinone, as follows:



$$2\ \begin{array}{ccccccc} CH_3 & - & C & - & CO & - & CHCl \\ & & \| & & & & | \\ & & HC & - & CO & - & CHCl \end{array} = \begin{array}{ccccccc} CH_3 & - & C & - & CO & - & CH \\ & & \| & & & & \| \\ & & HC & - & CO & - & CCl \end{array} + \begin{array}{ccccccc} CH_3 & - & C & - & CO & - & CCl \\ & & \| & & & & \| \\ & & HC & - & CO & - & CH \end{array} + 2HCl.$$

p-Chlortoluquinone.

m-Chlortoluquinone.

---

[1] This Journal **13**, 423.

Preparation of Quinones.—In the work described below, the ordinary methods of preparing quinones by oxidation with potassium (or sodium) dichromate were often found unsatisfactory. A simpler way to obtain these bodies, and one which is generally applicable, is to oxidise the corresponding hydroquinone, or often an amido-compound, by means of manganese dioxide and sulphuric acid in moderate excess. By brisk distillation with steam the quinone is quickly driven over, and can be at once obtained pure, and in very satisfactory quantity, from the well-cooled first portions of the distillate. When necessary, the filtrate, together with the less saturated portions of the distillate, can be extracted with ether in the usual way, and a small amount more of the substance obtained. The yield by this method is 50–60 per cent. of the calculated amount, and the troublesome emulsions and purifications of other processes are avoided. As this is by far the best way to obtain benzoquinone in quantity, and is frequently referred to below, the details of the process are given here.

Benzoquinone.—Upon the fresh mixture of 5 parts hydroquinone and 6 parts of powdered manganese dioxide, in a capacious flask, pour about 28 parts warm dilute sulphuric acid containing 7 parts ordinary acid. Mix well, and immediately distil briskly with steam, through a condenser, into a receiver kept as cold as possible by water containing salt and chopped ice. It is well to have the condenser warm at first to prevent clogging. Also, as the reaction at first is rather violent, the steam should be well under control, and the connection with the generator should be a loose one which can instantly be broken. The supersaturated part of the distillate is well cooled and the crystalline solid filtered off and dried by pressing well between bibulous paper. Fifty per cent. of the theoretical yield can thus be obtained in one to three hours. In the case of benzoquinone it is unprofitable to work up the ice-cold filtrate and the rest of the colored distillate, which together contain 5–10 per cent. more.

This method works well with relatively large quantities and is recommended for the manufacture of quinone. The difference in price between it and hydroquinone[1] should be greatly diminished thereby. On the large scale the saturated aqueous solution and the excess of manganese dioxide could be used for another lot.

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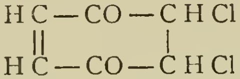
[1] Kahlbaum (October, 1891) lists: quinone, 100 grams, 20 marks; hydroquinone, 100 grams, 2 marks.

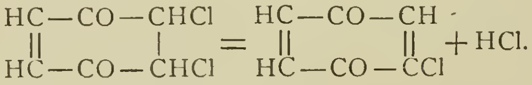
I.—BENZOQUINONE ADDITION-PRODUCTS.

Quinone dichloride, 

$\begin{array}{ccccc} HC & - & CO & - & CHCl \\ \| & & & & | \\ HC & - & CO & - & CHCl \end{array}$

.—This substance is prepared as follows: 10 grams of quinone are dissolved in about 60 grams of dry chloroform in a 200-cc. flask, and into the solution, kept cold by surrounding it by ice and salt, is admitted a lively stream of dry chlorine. Moisture is excluded by stopping the flask with a doubly perforated cork, through one hole of which passes a wide tube, connected with the chlorine generator, and through the other an exit tube for escaping gases, protected at the top by calcium chloride. The chlorine is rapidly absorbed by the quinone solution, and in about ten minutes, during which the flask is shaken gently, crystalline quinone dichloride begins to separate out. After forty minutes the flask is detached and its contents washed with chloroform and dried on clay plates. If necessary, the product is purified by dissolving in fuming nitric acid and precipitating with water, but this step is usually superfluous.

Thus prepared, quinone dichloride is obtained as a pale yellowish-white, tasteless, nearly odorless, crystalline powder, melting at 146°[1] to a clear amber liquid, which decomposes in the capillary tube at about 185°. In the solid state it is very stable, subliming readily without decomposition. Recrystallised from glacial acetic acid it is obtained in thin, colorless, transparent plates. It is quite soluble in warm glacial acetic acid and in warm alcohol, but too much heating, especially in presence of water, decomposes it, hydrochloric acid being split off with ease. The light greenish-yellow solution, on warming with addition of a little water, darkens, and on cooling, fails to yield crystals. On extracting with ether, reddish-yellow rhombic crystals of monochlorquinone (melting-point 57°) are obtained:



$$\begin{array}{ccccc} HC & - & CO & - & CHCl \\ \| & & & & | \\ HC & - & CO & - & CHCl \end{array} = \begin{array}{ccccc} HC & - & CO & - & CH \\ \| & & & & \| \\ HC & - & CO & - & CCl \end{array} + HCl.$$

---

[1] The melting-points given in this paper, other than those quoted, may be regarded as "corrected." For those above 100° an apparatus enclosing the whole mercury column of a good thermometer, was employed, and all were frequently checked by comparative determinations with a standard set of Gerhardt's short thermometers. *e.g.* hydroquinone (melting-point 169°, uncorrected) melted in the apparatus used at 172°-172.5°; with Gerhardt's thermometer (145°-210°), at 172.5°-173°. The calculated correction was 3.7°.

The general action of reagents is likewise to split off hydrochloric acid. Benzene and acetone also dissolve it, and ether sparingly, but the safest solvent is chloroform, of which about twenty parts of hot, thirty at ordinary temperature, and a third more at 0°, are required. It dissolves without change in warm fuming nitric acid, and separates from concentrated solutions on cooling or diluting with water. Alkalies instantly decompose it like other halogen addition-products of quinone, forming a dark brown solution; the solid, when first touched with the alkali, turning dark bluish-green. Zinc and acetic acid convert it into hydroquinone.

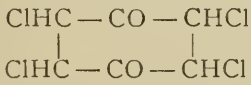
Prepared as above, the yield of pure dichloride was uniformly 75–80 per cent. of the theoretical. Dried over sulphuric acid, it was analysed with the following results:

0.2098 gram substance gave 0.3068 gram CO_2 and 0.0426 gram H_2O.

0.2696 gram substance gave 0.4333 gram AgCl (Carius).

	Theory for $C_6H_4O_2Cl_2$.	Found.
C	40.22	39.89
H	2.23	2.25
Cl	39.67	39.76

Quinone tetrachloride,



$$\begin{array}{l} \mathrm{ClHC-CO-CHCl} \\ \;\;\;| \qquad\qquad\quad | \\ \mathrm{ClHC-CO-CHCl} \end{array}$$

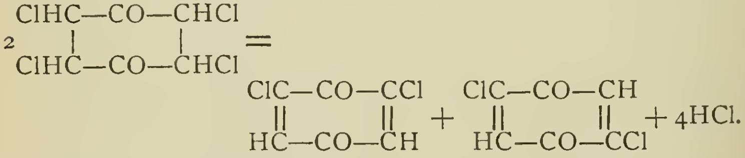
.—This substance was prepared by dissolving quinone dichloride in about forty parts of dry chloroform, cooling and passing dry chlorine rapidly for 20–30 minutes, using the apparatus employed in the preparation of the dichloride. After standing some time in the cold, and rubbing the side of the flask with a glass rod, the tetrachloride begins to separate slowly. Standing at higher temperature hastens this formation somewhat, but also favors secondary reactions. In any case, a large quantity of hydrochloric acid is given off and the yield is small: *e. g.*, 8 grams of quinone dichloride dissolved in chloroform (300 grams) and treated with chlorine thirty minutes at 0°, on standing two hours in the cold and another hour at ordinary temperature, gave but 1.8 grams of tetrachloride. After washing with chloroform and drying on clay plates, the substance was treated with fuming nitric acid, washed, and again dried, finally over sulphuric acid in a vacuum.

0.2338 gram gave 0.2450 gram CO_2 and 0.0340 gram H_2O.
0.2520 gram gave 0.5708 gram AgCl (Carius).
0.1443 gram gave 0.3268 gram AgCl (Carius).

	Theory for $C_6H_4O_2Cl_4$.	Found. I.	Found. II.
C	28.80	28.60	...
H	1.60	1.62	...
Cl	56.80	56.06	56.07

Quinone tetrachloride crystallises from chloroform in pure white microscopic prisms; recrystallised from glacial acetic acid, it occurs as colorless, transparent flat needles. It is odorless, and practically insoluble, in the cold, in ordinary solvents—glacial acetic acid, alcohol, ether, chloroform, and benzene dissolving it but sparingly. The small amount dissolved by hot fuming nitric acid is precipitated unchanged on diluting with water. Heated in a test-tube it sublimes, without melting, in rosettes of microscopic leaves or prisms; in a capillary it darkens slightly about 185°, and often sublimes without melting at 236°. Usually, however, it melts with decomposition, more or less sharply, at 226°, to a reddish-brown liquid.

On warming with dilute alcohol it loses hydrochloric acid, giving meta- and paradichlorquinone according to the equation:



$$2\begin{array}{l}\mathrm{ClHC{-}CO{-}CHCl}\\ \;\;|\qquad\qquad\;\; |\\ \mathrm{ClHC{-}CO{-}CHCl}\end{array} = \begin{array}{l}\mathrm{ClC{-}CO{-}CCl}\\ \;\|\qquad\qquad\;\|\\ \mathrm{HC{-}CO{-}CH}\end{array} + \begin{array}{l}\mathrm{ClC{-}CO{-}CH}\\ \;\|\qquad\qquad\;\|\\ \mathrm{HC{-}CO{-}CCl}\end{array} + 4\mathrm{HCl}.$$

The tetrachloride is, however, less easily split than the corresponding tetrabromide,[1] and as the hydrochloric acid split off can also react on the quinones formed, it is a somewhat delicate operation to accomplish the above change quantitatively. It was found best to boil for about 5 minutes and then pour into water and treat the precipitate, which contained unchanged tetrachloride, with a small amount of ether. The ethereal solution yielded on fractional crystallisation, two bodies. The less soluble one, melting at 157°, was paradichlorquinone; the more soluble, which was not yet quite free from the para-compound, melted at

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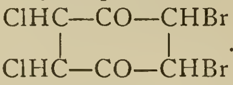
[1] Nef: This Journal 12, 486.

104°–106°, but was unquestionably metadichlorquinone[1] (melting-point 120°).

On treating quinone tetrachloride with zinc dust and acetic acid in the cold it is converted into pure hydroquinone.

Quinone dichloride-dibromide,  $\begin{array}{ccccc} \mathrm{ClHC} & — & \mathrm{CO} & — & \mathrm{CHBr} \\ | & & & & | \\ \mathrm{ClHC} & — & \mathrm{CO} & — & \mathrm{CHBr} \end{array}$.—If to a cool concentrated solution of quinone dichloride in chloroform the calculated amount of bromine is added, and the mixture is allowed to stand in the cold, no reaction is apparent for some time. The color produced by the first drop of bromine persists and no rise of temperature is noticed. After a while, however, the color of the solution is appreciably lighter, and white flakes begin to separate, and continue to do so for an hour or more, if the solution is allowed to attain the temperature of the room, and the side of the flask is rubbed with a glass rod. Meanwhile, and for some hours after, no acid fumes make their appearance, and if the filtrate is set aside the dichloride-dibromide continues to crystallise out for several days, accompanied by but slight evolution of hydrobromic acid.

Quinone dichloride-dibromide was prepared in this manner, and, like the tetrachloride, washed with chloroform, treated with warm fuming nitric acid, washed with cold conc. nitric acid, then with water, and dried on clay plates. From 8 grams dichloride 4.6 grams were obtained.

0.3032 gram substance, dried over sulphuric acid in vacuum, gave 0.2389 gram CO_2 and 0.0315 gram H_2O.

0.2500 gram substance gave 0.4884 gram AgCl and AgBr (Carius).

	Theory for $C_6H_4O_2Cl_2Br_2$.	Found.
C	21.24	21.49
H	1.18	1.15
Cl	20.94	68.07
Br	47.20	

Thus prepared, quinone dichloride-dibromide is a white crystalline body melting at 202°–203° with decomposition, and subliming to leafy rosettes. In solubility it is like the tetrachloride. It is decomposed on heating in dilute acetic acid or alcohol, but is stable in dry chloroform, being unchanged after standing three weeks in this solvent. Reduced with zinc and acetic acid, it is converted into hydroquinone.

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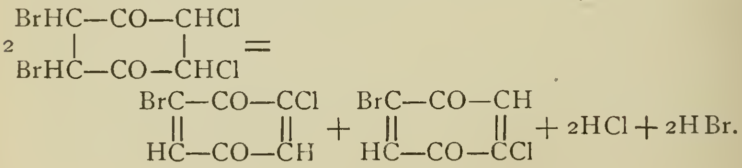
[1] The analogous decomposition has been carried out more carefully in the case of the dichloride-dibromide, and by Nef in case of the tetrabromide. The melting-point of the meta-compounds was always found low at first, owing to the presence of the para-product. To get it entirely free from the para-compound is a matter of much difficulty, requiring considerable material and repeated crystallisation. In this work, however, the melting-points invariably went up, and never was there a sign of a still lower melting ortho-compound. (*Cf.* also the behavior of meta- and para-chlor- and brom-toluquinones.)

Decomposition of Halogen Addition-products of Quinone by Heating in Solution.

As already stated, this decomposition is analogous in all cases. That of the dichloride-dibromide was the most carefully studied. 4.2 grams of this substance were warmed gently with common alcohol until a clear, amber-colored solution was obtained, a small amount of water (5–10 per cent.) was then added, and warming continued for a short time. On pouring the resulting brownish-yellow solution into 2–3 volumes of water a copious yellow precipitate was obtained which, filtered, washed with water and dried, weighed 2.2 grams. The filtrate and washings, on extracting with ether, gave a little more, making the yield a theoretical one. A low temperature seems essential, for, in other experiments, at boiling temperatures, secondary reactions apparently took place, yielding soluble products.

The yellow product dissolved with great ease in warm absolute ether, and on standing there were deposited two kinds of crystals which, by fractional crystallisation from a mixture of ordinary and petrolic ethers, were separated. The less soluble, compact crystals are identical with the chlorbromquinone obtained by Levy and Schultz.[1] The others, long straggly fibers, are metachlorbromquinone. Comparison of these products with the synthetical preparations (pp. 563 and 565) established their identity. A determination of the halogens in each by Carius' method gave 52.18 per cent. and 52.45 per cent. respectively, instead of the calculated 52.15 per cent. The following reaction has therefore taken place in the decomposition of quinone dichloride-dibromide:



$$2\begin{array}{l}\mathrm{BrHC{-}CO{-}CHCl}\\ \quad|\qquad\qquad|\\ \mathrm{BrHC{-}CO{-}CHCl}\end{array} = \begin{array}{l}\mathrm{BrC{-}CO{-}CCl}\\ \quad\|\qquad\qquad\|\\ \mathrm{HC{-}CO{-}CH}\end{array} + \begin{array}{l}\mathrm{BrC{-}CO{-}CH}\\ \quad\|\qquad\qquad\|\\ \mathrm{HC{-}CO{-}CCl}\end{array} + 2\mathrm{HCl} + 2\mathrm{HBr}.$$

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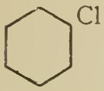
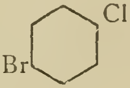
[1] Ann. Chem. (Liebig) **210**, 160; Ber. d. chem. Ges. **15**, 656.

Synthetic Preparation of Parabromchlorquinone.

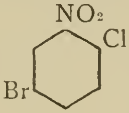
Since meta- and parabromchlorquinone have not yet been isolated, it was necessary to synthesise these two compounds and prove their identity with the decomposition-products of quinone dichloride-dibromide. The parabromchlorquinone was prepared from pure benzene by the following five steps:



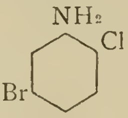
I.



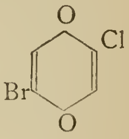
II.



III.



IV.



V.

The products I–III are known compounds.

Amidoparabromchlorbenzene.—Parabromchloraniline (IV) was prepared from the nitro-body (III)[1] by reduction with zinc and acetic acid. Ten grams nitroparabromchlorbenzene were dissolved in warm glacial acetic acid and 10–20 per cent. water added, but not in sufficient quantity to cause precipitation. To the hot solution was then added gradually, but as rapidly as was practicable, zinc dust, until the reaction was complete. The colorless solution was filtered hot, and the filtrate diluted and extracted with ether. After neutralising with sodium hydroxide, again extracting, and drying with stick potash, there separated on standing a considerable quantity of long, hard, yellowish-red needles in tufts and bunches. Other reduction-methods gave this azo-body as the chief product. It melts about 220° and is very sparingly soluble in water, ether, and alcohol. After filtering and distilling off the ether, the residue was distilled under diminished pressure. At about 170° under a pressure of 55 mm., 6 grams parachlorbromaniline distilled over, clear yellow at first, then slightly reddish, and solidified, on cooling, in a nearly white crystalline cake, while considerable of the azo-body remained behind.

Recrystallised from hot water (in which it is very sparingly soluble), fine, silky, white needles were obtained melting at 44.5°. Alcohol and ether dissolve the substance quite readily. Long standing with water decomposes it.

0.1980 gram, dried over sulphuric acid in a vacuum, gave 0.2514 gram CO_2 and 0.0478 gram H_2O.

0.2231 gram gave 0.3588 gram AgCl,AgBr (Carius).

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[1] Körner: Jahresbericht, 1875, 327.

	Theory for $C_6H_3ClBr(NH_2)$.	Found.
C	34.87	34.63
H	2.42	2.68
Cl } Br }	55.93	56.03

Hydrochloride of parabromchloraniline, $C_6H_3ClBr(NH_2),HCl + H_2O$.—The free base, dissolved in hot hydrochloric acid, yielded on standing, inch-long prisms with rhombic section, melting at 196°. The hydrochloride is less soluble in alcohol than the free base and far more soluble in hot water, but much heating with water partially decomposed it. A determination of HCl by precipitating AgCl from the aqueous solution, acidified with nitric acid, gave 14.10 per cent. HCl. Theory for the salt with one molecule crystal water, 13.99 per cent. (0.3685 gram substance gave 0.2032 gram AgCl.)

Sulphate of parabromchloraniline, $[C_6H_3ClBr(NH_2)]_2,H_2SO_4$. This salt crystallised from a hot solution of the base in dilute sulphuric acid in white ill-formed prisms or flat needles. Dried over sulphuric acid, dissolved in hot water containing hydrochloric acid, and digested several hours with barium chloride in slight excess, 0.1335 gram of the substance gave 0.0612 gram $BaSO_4$, corresponding to 19.27 per cent. H_2SO_4, instead of 19.18 per cent. required by theory.

Parabromchlorquinone.—After an unsatisfactory attempt to oxidise the amidoparabromchlorbenzene with sodium dichromate according to Nietzki's method for preparing ordinary quinone,[1] the following procedure gave excellent results. To 5 grams of the parabromchloraniline dissolved in about 150 cc. hot dilute sulphuric acid, 40 grams manganese dioxide were added and the mixture immediately distilled with steam. A beautiful yellow quinone-like body at once separated from the distillate, clogging the tube of the condenser, and more was obtained by extracting the distillate with ether.

This body is identical with one obtained from heating quinone dichloride-dibromide with dilute alcohol (see p. 560), as is shown by comparing the properties of the two.[2] The decomposition-product melted at 174°, the synthetic at 175°. Both have the same orange-yellow color and pungent, musty odor. They are soluble in ether, less in ligroin, alcohol, and water, and more in chloroform, from which they crystallise in small rhombic plates. These, optically, are strongly doubly refractive and exhibit a remarkable pleochroism (yellowish-white, dark yellow). They belong to the monoclinic system. The acute angle of the rhombic face was measured approximately and found to be, in both, 56°–57°.

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[1] Ber. d. chem. Ges. 19, 1467.

[2] It follows also that the product obtained by Levy and Schultz (*loc. cit.*) by treating chlorquinone with hydrobromic acid is *para*bromchlorquinone, since it corresponds in its properties with the above products.

Analysis of synthetic (I) and decomposition (II) products:

I. *a*. 0.2203 gram synthetic product gave 0.2646 gram CO_2 and 0.0203 gram H_2O.

I. *b*. 0.2160 gram synthetic product gave 0.3240 gram AgCl, AgBr, which by reduction gave 0.2107 gram Ag.

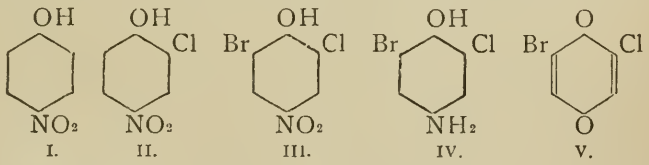
II. 0.2102 gram decomposition-product gave 0.3148 gram AgCl,AgBr, which by reduction gave 0.2044 gram Ag.

Theory for Ag in AgCl,AgBr found is 0.2110 and 0.2049 gram respectively.

	Theory for $C_6H_2ClBrO_2$.		Found.	
		I*a*.	I*b*.	II.
C	32.51	32.76	...	...
H	0.90	1.02	...	...
Cl	16.03 } 52.15	...	52.26	52.18
Br	36.12 }			

Synthetic Preparation of Metabromchlorquinone.

Starting with paranitrophenol of Kahlbaum's manufacture, the steps in this synthesis are represented by the following formulæ:



Chlornitrophenol (II) was prepared by chlorinating paranitrophenol in an exhausted flask with potassium chlorate.[1] The melting-point (111°) and other properties corresponded to those given by Kollrepp.

Metabromchlorparanitrophenol (III).—A solution of chlornitrophenol in warm glacial acetic acid was diluted with an equal volume of water, and to it, while constantly shaking, the calculated amount of bromine was slowly added. The bromine was readily absorbed, and when about half had been added, white crystals appeared and increased in quantity to the end. These were filtered off, dried on clay plates and then at 100°. They were practically pure, melted at 139.5°, and when analysed gave the following figures:

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[1] Kollrepp: Ann. Chem. (Liebig) 234, 3.

0.2206 gram substance gave 0.2270 gram CO_2 and 0.0250 gram H_2O.

0.2530 gram substance gave 0.3347 gram AgCl,AgBr (Carius).

	Theory for $C_6H_2BrClNO_2OH$.	Found.
C	28.51	28.06
H	1.19	1.26
Cl Br	45.74	46.08

Metabromchlorparaamidophenol (IV).—The above nitro-body, reduced with tin and conc. hydrochloric acid, gave a tin double salt of the corresponding amido-compound, which separated out almost completely from the concentrated acid solution, on cooling, in long, silky, white needles melting at 228°. It was filtered off, dried, dissolved in water, and the tin precipitated by hydrogen sulphide. The hydrochloride was converted into the sulphate by addition of sulphuric acid and evaporation. The latter salt crystallises in silky, white needles soluble in hot but nearly insoluble in cold water, and melts at 221°. The analysis gave unsatisfactory results, as only 16.50 per cent. H_2SO_4 was obtained, instead of 18.05 demanded by theory. The free base was therefore isolated by adding sodic carbonate to the hot aqueous solution of the sulphate. It came down in brownish-white prisms, and after recrystallisation from benzene was obtained in long, colorless needles. The analysis, however, gave low results in carbon, which, possibly, may be due to the fact that the substance burns with difficulty. No further work was done in this direction, as the product was not an essential, but simply an intermediate one.

Metabromchlorquinone (V).—The oxidation of metabromchlorparaamidophenol was effected, as in the para-series, by adding 8 parts manganese dioxide to a solution of the sulphate in dilute sulphuric acid and immediately distilling with steam. The yield is good, and the larger part of the product separates from the cooled distillate in soft masses of yellow needles with the characteristic odor.

This product resembles in every respect one obtained by heating the quinone dichloride-dibromide except that the latter melted 0.5°–1° lower, namely, about 114°. The synthetic product melted at 114°–115°. Both have a pungent, musty odor and crystallise from hot water in sulphur-yellow, fibrous needles. They sublime on heating and are very volatile with steam. They are very soluble in ether, less so in ligroin, alcohol, and water.

The following figures were obtained from analysis:

I*a*. 0.3054 gram synthetic product gave 0.3612 gram CO_2 and 0.0249 gram H_2O.

I*b*. 0.2232 gram synthetic product gave 0.3354 gram AgCl, AgBr (Carius).

I*c*. 0.2367 gram synthetic product gave 0.3558 gram AgCl, AgBr (Carius),—

which, reduced by hydrogen, gave $\left\{\begin{matrix}0.2165\\0.2300\end{matrix}\right\}$ gram Ag.

Theory for these quantities AgCl,AgBr $\left\{\begin{matrix}0.2185\\0.2318\end{matrix}\right\}$ gram Ag.

II. 0.2192 gram decomposition-product (p. 560) gave 0.3300 gram AgCl,AgBr and 0.2165 gram Ag.

(Theory: 0.2150 gram Ag.)

	Theory for $C_6H_2ClBrO_2$.	Found.			
		I*a*.	I*b*.	I*c*.	II.
C	32.51	32.26	...	...	...
H	0.90	0.91	...	...	...
Cl Br	52.15	...	52.35	52.37	52.45

II.—TOLUQUINONE ADDITION-PRODUCTS.

Preparation of toluquinone.—Several attempts to obtain this body from orthotoluidine by oxidising it with potassium dichromate[1] gave unsatisfactory results, owing to the persistent emulsion which forms when the oxidised mixture is shaken with ether, and to the impurity of the extracted product.

A fair yield of pure substance can be quickly obtained by oxidising with manganese dioxide in the manner described above (page 555). On passing steam into a mixture of 140 grams manganese dioxide and 40 grams orthotoluidine dissolved in dilute sulphuric acid (160 grams acid and 480 grams water), contained in a flask capable of holding three or four liters, toluquinone will pass over with a small quantity of distillate, and crystallise out, on cooling, in yellow plates melting at 68°–69°. By extracting the filtrate from this product, and the later portion of the yellow distillate, with ether, drying the ethereal solution with calcium chloride, and distilling at a low temperature, or quickly driving off the ether in the cold by a stream of dry air, about one-fourth more can be obtained.

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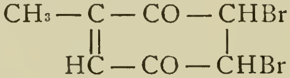
[1] Schniter: Ber. d. chem. Ges. **20**, 2282.

The quantities given yielded 13.3 grams pure toluquinone in about an hour and 3.2 grams more on extracting. Should a portion of the contents of the flask be carried over by the vigorous frothing which sometimes takes place, the whole distillate can be treated with ether, but if the substances are well mixed and the steam is under control this can be prevented.

Toluquinone dibromide,  $\begin{array}{ccccccc} CH_3 & - & C & - & CO & - & CHBr \\ & & \| & & & & | \\ & & HC & - & CO & - & CHBr \end{array}$.—If to a cold solution of toluquinone in about three parts dry chloroform the calculated quantity of bromine is added, decoloration of the bromine takes place immediately, without evolution of hydrobromic acid. Spontaneous evaporation from a wide dish leaves a mass of light-yellow, flat needles of toluquinone dibromide. When dry these turn green, but washing with small quantities of alcohol leaves the body yellow. Also by dissolving in a mixture of concentrated and fuming nitric acids and pouring into ice-water, a light-yellow, crystalline powder is obtained which is pure. The yield is about 70 per cent.

0.2694 gram substance, dried over sulphuric acid in a vacuum, gave 0.2932 gram CO_2 and 0.0512 gram H_2O.

0.3150 gram substance gave 0.4212 gram AgBr (Carius).

	Theory for $C_7H_6O_2Br_2$.	Found.
C	29.78	29.68
H	2.13	2.11
Br	56.74	56.90

Toluquinone dibromide closely resembles benzoquinone dibromide[1] in appearance and properties, but it is more stable. It melts at 61°–62°, and sublimes at a higher temperature. It dissolves in alcohol, ether, chloroform, acetic acid, and somewhat in ligroin. Slowly soluble in ordinary nitric acid, the fuming acid dissolves it quite freely, and water precipitates the greater part from either solution. Heated in dilute alcohol or acetic acid solution, it breaks down into meta- and parabromtoluquinone (see below). This proves the constitution of the dibromide to be as given above. Reduced in the cold with zinc dust and acetic acid, it is converted into hydrotoluquinone (melting-point 125°).

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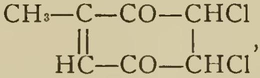
[1] Nef: This Journal **12**, 483.

On treating the dibromide in the cold with the theoretical quantity of bromine, no change was perceptible after twenty hours. Another mixture of the dibromide and bromine, with a little iodine added, was boiled with an inverted condenser for some time before any action took place, then copious acid fumes were evolved and a white solid separated, which, filtered off and crystallised from alcohol, melted at 203°. Oxidised by nitric acid, this gave a yellow, quinone-like body melting at about 234°. These bodies are probably tribromhydrotoluquinone and tribromtoluquinone respectively. Canzoneri and Spica,[1] by the action of bromine, iodine and *water* on toluquinone, obtained tribromtoluquinone mixed with a little dibromtoluquinone (melting-point 83°). They give as the melting-point of the first 235°, and of the hydroquinone that they got from it, 201°–202°. In this case the formation of quinones was doubtless due to the presence of water and the consequent oxidising action of the bromine.

Toluquinone dichloride,



$$\begin{array}{l} CH_3—C—CO—CHCl \\ \quad\;\;\, \| \qquad\qquad\;\; | \\ \quad\; HC—CO—CHCl \end{array}$$

, was made in the same manner as benzoquinone dichloride, by treating a solution of toluquinone in about four parts of dry chloroform, in the cold, with dry chlorine gas; but the reaction is slower and often incomplete, consequently the yield was usually not so great. By recrystallising from hot chloroform several times, a pure product was obtained, which, dried in a vacuum-desiccator over sulphuric acid and analysed, gave the following results:

0.1627 gram gave 0.2578 gram CO_2 and 0.0453 gram H_2O.
0.2387 gram gave 0.3566 gram AgCl (Carius).

	Theory for $C_7H_6O_2Cl_2$.	Found.
C	43.52	43.21
H	3.11	3.09
Cl	36.79	36.93

This body is perfectly analogous to its lower homologue. Its greater stability, however, allows it to be purified by repeated crystallisation from hot chloroform. In this case also the chlorine-saturated solution from which the toluquinone dichloride first separated, can be made to yield more by direct evaporation. Evaporation of the benzoquinone-dichloride filtrate, on the other hand, causes substitution of the chlorine, and a complex mixture of solids is left. On boiling it in dilute alcoholic or acetic-acid solution, toluquinone dichloride is converted into meta- and para-chlortoluquinone (see below). This proves the constitution of the substance to be as given above. Reduced with zinc and acetic acid, it yields hydrotoluquinone. It is a cream-white, crystalline body, which melts at 135°–136° to an amber-yellow liquid, and decomposes in the capillary tube at about 164°. Heated in a test-tube, it sublimes apparently unchanged, like the di- and tetrachloride of quinone.

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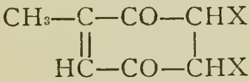
[1] Ber. d. chem. Ges. **16**, 793.

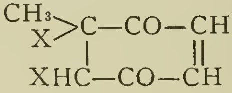
Decomposition-products of Toluquinone Dibromide and Dichloride.

It is evident that the addition of halogen (X_2) to the toluquinone can take place in two, or in one of two ways,



$$\begin{array}{ccccc} CH_3{-}C & - & CO & - & CHX \\ \| & & & & | \\ HC & - & CO & - & CHX \end{array}$$

A.



$$\begin{array}{ccccc} {}^{CH_3}_{X}{>}C & - & CO & - & CH \\ | & & & & \| \\ XHC & - & CO & - & CH \end{array}$$

B.

where *A* represents an addition to the ethylene side of the molecule, and *B* to the propylene side. The addition-product *B* can lose halogen-hydride (HX) in but one way, and must then form an ortho-halogenated toluquinone, whereas the product *A* can lose halogen hydride in two ways, and give a meta- and a para-halogenated toluquinone (see reaction p. 554). It becomes thus an easy matter to determine the constitution of the toluquinone dibromide and dichloride described above; it is simply necessary to determine the nature of the decomposition-products.

1. *Toluquinone dibromide.*—The substance was dissolved in 85 per cent. alcohol and warmed for about 10 minutes on a water-bath, or till the solution turned brownish red. On pouring into two volumes of water a copious separation took place, either of yellow flakes or of a brownish oil which soon solidified. The yield was almost a theoretical one. On crystallising from water, alcohol, or from a mixture of ether and ligroin, long, prismatic yellow needles were obtained. Although more or less rough

under the microscope, these appeared perfectly homogeneous and melted sharply at 68°; there were left, however, a few unmelted particles. Repeated crystallisation from ligroin soon made it apparent that two substances were present; and by mechanical separation, thin, flat needles melting at 94°–95°, and compact, prismatic crystals melting at 105°–106°, were finally obtained. These melting-points correspond closely with those given for meta- (93°)[1] and for Schniter's bromtoluquinone (105°).[2]

A pretty sharp separation of the two isomers formed was at last accomplished by converting the mixture into the corresponding hydrotoluquinones. Parabromhydrotoluquinone was found to be far less soluble in water and in a mixture of ether and ligroin, than the meta-compound. Both are already known: the melting-point of the latter is given as 112°,[1] that of the former about 160°.[3] Reduction was effected by means of warm aqueous sulphurous acid, and the resulting light-yellow solution gave, on standing over night, white fibrous crystals like sal ammoniac. These, repeatedly crystallised from a mixture of ether and ligroin, gave a substance melting well at 176° (instead of 160.° See footnote below). This is parabromhydrotoluquinone. Oxidised with ferric chloride it gives parabromtoluquinone (melting-point found, 107°), and it behaves like the product obtained from the action of hydrobromic acid on toluquinone. The above aqueous solution extracted with ether, as well as the ether-ligroin mother-liquors from the para-compound, gave white leaflets which, though persistently recrystallised, melted at about 108°. On oxidising with ferric chloride, however, beautiful yellow needles melting at 94°–95° were obtained. It follows, therefore, that the product is metabromhydrotoluquinone. As Claus and Jackson give as the melting-point for this body 112°, it is highly probable that the above substance still contained traces of the para-compound, which it was not possible, in this case, to completely eliminate (*cf.* footnote, p. 559).

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[1] Claus and Jackson: J. prakt. Chem. [2] **38**, 326–7.

[2] Ber. d. chem. Ges. **20**, 2286.

[3] Ibid. The body obtained by Schniter was, without doubt, impure parabromhydrotoluquinone, but the melting-point he gives is nearly 20° too low. His substance may have contained a little metabromhydrotoluquinone or gummy matter (*cf.* p. 573). On repeating his experiment at 0° (allowing aqueous hydrobromic acid to act on toluquinone for two days) there was obtained a light-colored body, which, crystallised from a mixture of ether and ligroin, gave a nearly white substance *melting sharply at* 179° with decomposition. The phenomena of this experiment were analogous to those observed when toluquinone was treated with hydrochloric acid (p. 573). In both cases the para-products thus obtained melted slightly higher than the reduction-products to be described.

The two hydroquinones, thus separated, were dried over sulphuric acid and their halogen contents determined by Carius' method.

I. 0.2898 gram of the para-compound gave 0.2673 gram AgBr.
II. 0.2067 gram of the meta-compound gave 0.1929 gram AgBr.

	Theory for $C_7H_7BrO_2$.	Found. I.	Found. II.
Br	39.41	39.25	39.71

2. *Toluquinone dichloride.*—This substance was heated in dilute alcoholic solution exactly as above in the case of the corresponding dibromide. On adding water, an almost quantitative yield of isomeric chlortoluquinones was obtained which could not be separated from each other. An analysis of the mixture, crystallised from ligroin and melting at 68°–86°, gave figures agreeing well for a chlortoluquinone.

0.1741 gram substance, dried over sulphuric acid, gave 0.1601 gram AgCl (Carius).

	Theory for $C_7H_5ClO_2$.	Found.
Cl	22.69	22.75

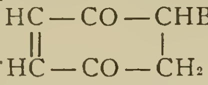
The separation of this mixture into its constituents was accomplished by means of the hydroquinones, exactly as in the case of the corresponding brom-compounds. In this way, thin, white needles melting at 172°–173°, and leaflets in bunches which melted at 105°–107°, were obtained. These correspond to para-[1] and to metachlorhydrotoluquinone[2] respectively, but the same difficulty was experienced here as in case of the brom-compounds, in getting an absolutely pure meta-product.

The two chlorhydrotoluquinones obtained were dried over sulphuric acid and the amount of chlorine in each was determined by Carius' method.

I. 0.1780 gram of para-body gave 0.1613 gram AgCl.
II. 0.1630 gram of meta-body gave 0.1482 gram AgCl.

	Theory for $C_7H_7ClO_2$.	Found. I.	Found. II.
Cl	22.39	22.41	22.48

III.—THE ACTION OF HALOID ACIDS ON QUINONES.

From the action of halogens on quinones, as shown above and in a previous paper by Nef,[3] it seemed highly probable that the action of haloid acids on quinones takes place in a similar manner. The ease with which quinone, for instance, forms a dibromide leads one to expect that it might form, with hydrobromic acid, a hydrobromide,  $\begin{array}{l} HC - CO - CHBr \\ \| \qquad\qquad\quad | \\ HC - CO - CH_2 \end{array}$, especially since olefine derivatives, as is well known, take up halogen hydrides with almost the same ease as halogens. Notwithstanding this, however, it can be shown that the behavior of quinones towards halogens and halogen hydrides is totally different.

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[1] Schniter (*loc. cit.* p. 2285) gives melting-point of his product as about 175°. *Cf.* p. 574 below.

[2] Melting-point 115°: Claus and Jackson (*loc. cit.* p. 328).

[3] This Journal **12**, 483.

My own experiments on the action of haloid acids on quinones are simply confirmatory of the results already obtained by Sarauw[1] and by Levy and Schultz.[2]

The Action of Hydrochloric Acid on Benzoquinone.

On passing *dry* hydrochloric acid into a 5-per cent. solution of quinone in dry chloroform, after two minutes much quinhydrone has separated out, and after about twenty minutes the mass is perfectly colorless, consisting of practically pure chlorhydroquinone melting at 106° and in theoretical amount. An entirely analogous result is obtained by using dry hydrobromic acid, except that in this case the resulting colorless mass is a mixture of bromhydroquinone (chief product) and para-dibromhydroquinone.

That the product formed at first in these two cases is quinhydrone was proved by filtering it off, washing well with chloroform and treating with hydrochloric acid. Although a Carius determination always gave 1–3 per cent. of halogen in this intermediate product, when suspended in chloroform and treated with dry hydrochloric acid it gave a mixture of nearly equal parts of chlorhydroquinone and hydroquinone. These results show that in the action of hydrochloric acid on quinone, one molecule of chlorine is set free according to the reaction:

$$\text{I.}\quad C_6H_4O_2 + 2HCl = C_6H_4(OH)_2 + Cl_2.$$

The resulting hydroquinone, before it can be acted upon by the chlorine set free, unites immediately with the quinone present in excess, forming quinhydrone, $C_6H_4(OH)_2,C_6H_4O_2$. The further action of the hydrochloric acid is to act on the quinone portion of the quinhydrone molecule, converting it into hydroquinone, and another molecule of chlorine is set free:

$$\text{II.}\quad C_6H_4(OH)_2,C_6H_4O_2 + 2HCl = 2C_6H_4(OH)_2 + Cl_2.$$

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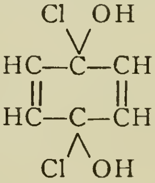
[1] Ann. Chem. (Liebig) **209**, 99.

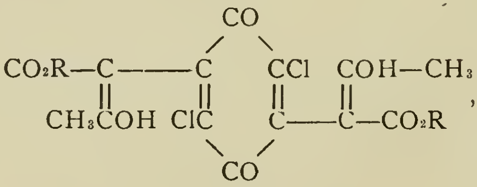
[2] *Ibid.* **210**, 133.

The chlorine set free in this last case (II) is only sufficient to convert one-half of the hydroquinone formed into chlorhydroquinone. Now pure quinhydrone when treated with hydrochloric acid is converted into equal molecules of hydroquinone and chlorhydroquinone. The same is true of the above intermediate product if it is filtered off from the chloroform solution, and consequently the solution must contain free chlorine (one molecule).

It follows therefore that quinone oxidises the hydrochloric acid, taking up its hydrogen to form hydroquinone and setting free chlorine. A number of new observations made by Dr. Nef[1] suffice to clear up this remarkable and enigmatic behavior of benzoquinone towards halogen hydrides.

Benzoquinone shows a twofold chemical behavior, owing to the fact that it contains, first, two ethylene groups, $\begin{array}{l}\mathrm{CH}—\\ \|\\ \mathrm{CH}—\end{array}$, which are reactive towards halogens; and secondly, two carbonyl groups, $\begin{array}{c}\mathrm{O}\\ \|\\ —\mathrm{C}—\end{array}$, which are reactive towards halogen hydrides and water. The action of hydrochloric acid on quinone, *e. g.*, is in the first place to form the addition-product  $\begin{array}{c}\mathrm{Cl}\quad\mathrm{OH}\\ \diagdown\!\diagup\\ \mathrm{HC—C—CH}\\ \|\qquad\quad\|\\ \mathrm{HC—C—CH}\\ \diagup\!\diagdown\\ \mathrm{Cl}\quad\mathrm{OH}\end{array}$, which immediately loses chlorine (one molecule), giving hydroquinone. The chlorine set free then reacts further on hydroquinone, giving chlorhydroquinone and hydrochloric acid.

That the above explanation is correct is made still more probable by some experiments since carried out in this laboratory by Dr. M. Ikuta. He had formerly obtained, by treating paradichlorquinone diaceto acetic ether,



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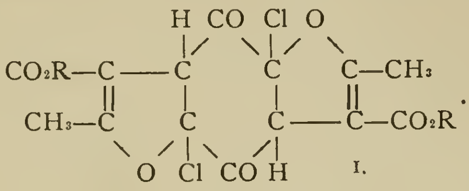
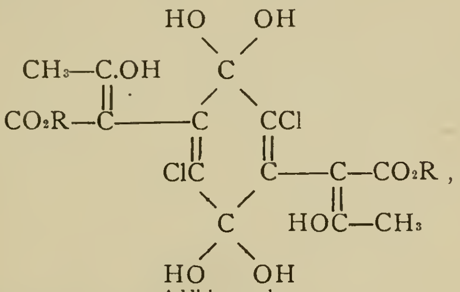
[1] Ann. Chem. (Liebig) **270**, 324.

with dilute sulphuric acid,[1] an isomer which he regarded as quinone-α-dimethyldifurfuran-β-dicarboxylic ether dihydrochloride,



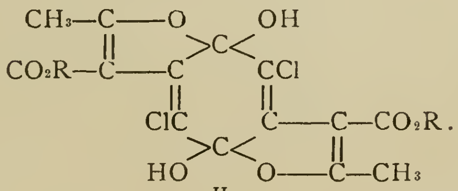
I.

It was supposed that two molecules of water had added themselves to the ethylene group in the quinone. In view of the results obtained by Nef it seems probable that the addition of water takes place at the carbonyl groups, as follows:



Addition-product.

which loses two molecules of water,



II.

The results obtained thus far point entirely towards formula II. because the substance dissolves unchanged in sodic hydrate.

The Action of Hydrochloric Acid on Toluquinone.

Schniter[2] has shown that, on treating toluquinone with concentrated hydrochloric acid, a chlorhydrotoluquinone is formed which melts at 175°. I also have studied the action of strong aqueous hydrochloric acid on this quinone and found that besides the para-compound, melting at 174–6°, some metachlorhydrotoluquinone is formed. Since in this reaction much gummy matter appears, more satisfactory results were obtained by passing *dry* hydrochloric acid into a cold 15-per cent. solution of toluquinone in chloroform, whereby the same phenomena were observed as in the case of quinone. On evaporating the chloroform and purifying the white residue by fractional crystallisation, first from water containing sulphurous acid and then from ligroin, much parachlorhydrotoluquinone (melting-point 176°) and some of the meta-compound (melting-point found 106–7°) were obtained. These products are identical with those described above (p. 570), and the same difficulty was experienced in isolating the more soluble body.

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[1] Jour. prakt. Chem. [2] **45**, 75.

[2] Ber. d. chem. Ges. **20**, 2285.

I. 0.2601 gram of the para-compound, dried over sulphuric acid, gave 0.2338 gram AgCl (Carius).

II. 0.1651 gram meta-compound gave 0.1505 gram AgCl.

	Theory for $C_7H_7ClO_2$.	Found.	
		I.	II.
Cl	22.39	22.23	22.54

IV.—ON QUINHYDRONES.

A few observations on quinhydrones were made that may possibly be of interest. Quinhydrone itself separates out in at least 91-per cent. yield on mixing ethereal or aqueous solutions of quinone and hydroquinone in equivalent amounts. In the former case it comes down in the form of dark green, irregular plates; in the latter, as bronze-green needles. All solvents dissociate it to some extent, especially those in which the two constituents are unequally soluble, as, for instance, chloroform. This is readily shown by the fact that the dry quinhydrone, which is odorless, instantly smells strongly of quinone when moistened with a solvent. On treating quinhydrone, suspended in dry chloroform, with dry hydrochloric acid until the mass is colorless, a mixture of equal molecules of hydroquinone and chlorhydroquinone results. These are readily separated by means of chloroform. In an experiment, 91 per cent. of the latter and 97.5 per cent. of the former substance was obtained.

Chlorquinhydrone.—Wichelhaus[1] obtained quinhydrone, and never a substituted quinhydrone, on bringing together, either quinone and a chlorinated hydroquinone, or hydroquinone and a chlorinated quinone. Chlorquinones, on the contrary, give chlorinated quinhydrones with their corresponding chlorhydroquinones[1]—in other words, no derivative of quinhydrone, $C_{12}H_{10}O_4$, containing an odd number of chlorine atoms is known.

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[1] Ber. d. chem. Ges. **12**, 1501–3.

The results which I have obtained in this direction seem to show a great difference according to whether quinone and a chlorinated hydroquinone be taken, or hydroquinone and a chlorinated quinone. In the former case a very complicated reaction sets in, whereas in the latter instance a chlorinated quinhydrone is actually formed.

Quinone and chlorhydroquinone.—On mixing chloroform solutions of these two substances (equal molecules), bronze-green scales separated out which, well washed, contained various quantities of chlorine but never over 3.5 per cent. Suspended in chloroform and treated with hydrochloric acid, these were converted into a mixture of hydroquinone (90 per cent.) and chlorhydroquinone (80 per cent.), and this proves that the product consisted chiefly of quinhydrone. The amount formed, however, was small, and another experiment was carried out with larger quantities and with absolute ether as the solvent. On mixing the ethereal solutions an immediate darkening was noticed, but no further change for an hour, and even after five hours' standing only a very slight amount of dark green needles had separated out. After three days the amount of this material had increased, but on filtering, it was found to be only one-fifth of the total possible. The mass obtained was of a dull, greenish-black color, and on analysis gave 6.46 per cent. chlorine. The ethereal filtrate when concentrated gave more of a similar substance, but in no case was the indication of a homogeneous substance at hand.

In order to determine the nature of the mixture, steam was passed into it and the quinones carried over. The residue contained, besides hydroquinones, much tarry matter which made the separation of the former a very difficult matter; but finally, by fractional crystallisation from benzene, the presence of much chlorhydroquinone and some hydroquinone was established. The volatile portion gave quinone in considerable amount and some chlorquinone.

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[1] Staedeler: Ann. Chem. (Liebig) **69**, 308, 314.

These results show that the action of quinone on chlorhydroquinone is very slow and complicated in its nature.

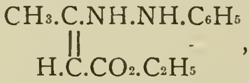
Chlorquinone and hydroquinone.—A marked difference is noticed here, compared with the case just mentioned. On mixing ethereal solutions containing equivalent quantities of chlorquinone and hydroquinone, the separation of a solid, although not immediate as in the case of quinhydrone (p. 574), begins after four or five minutes and continues uniformly. After twenty minutes, 50 per cent. of the entire material used was obtained by filtering and washing with a small quantity of ether. The substance obtained consisted of bronze-yellow, metallic needles, which appeared perfectly homogeneous. A determination of the halogen, according to Carius, gave 13.08 per cent. chlorine; theory for a monochlorquinhydrone, $C_{12}H_9ClO_4$, being 14.06 per cent. The somewhat low percentage of chlorine found may be due to a slight dissociation of the quinhydrone in the washing with ether. At any rate, this substance appears to be as easily split as ordinary quinhydrone, and as the more soluble constituent in this case is chlorquinone, it would be removed in larger quantity. This explanation is the more plausible because, on washing the material obtained with larger quantities of ether, the amount of the halogen constituent of the substance left was lessened.

The results thus point to the existence of a quinhydrone of the formula $C_6H_4(OH)_2,C_6H_3ClO_2$.

THE CONDENSATION-PRODUCTS OF ACETACETIC-ETHER HYDRAZIDE AND OF OXALACETIC-ETHER HYDRAZIDE.

By Charles Walker.

That acetacetic ether reacts with phenylhydrazine, forming a hydrazide of the constitution



$$\begin{array}{l} CH_3.C.NH.NH.C_6H_5 \\ \quad \| \\ H.C.CO_2.C_2H_5 \end{array}$$

, has been proved with all precision by the experiments of Nef.[1] This hydrazide, according to the conditions employed, can undergo various condensations: *e. g.*, (*a*) Knorr[2] has shown that it readily loses alcohol (one molecule), forming (1)phenyl(3)methyl(5)pyrazolon,[1]

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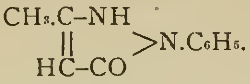
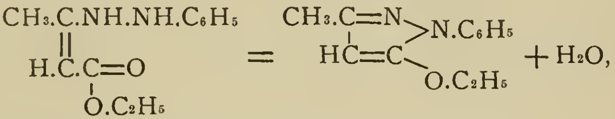
[1] Ann. Chem. (Liebig) **266**, 74.

[2] *Ibid.* **237**, 147.



$$\begin{matrix}CH_3.C\text{–}NH\\ \|\\ HC\text{–}CO\end{matrix}>N.C_6H_5.$$

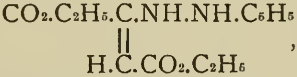
(*b*) Nef has shown that when treated with concentrated sulphuric acid it loses one molecule of ammonia, forming an indol derivative.[2] I have continued the study of this subject under the direction of Dr. Nef, and have found that the indol derivative formed is ethylic α-methylindol-β-carboxylate. (*c*) Furthermore, it was found that acetacetic-ether hydrazide, under still different conditions, reacts yet in another way, losing one molecule of water, as follows:



$$\begin{matrix}CH_3.C.NH.NH.C_6H_5\\ \|\\ H.C.C{=}O\\ |\\ O.C_2H_5\end{matrix} = \begin{matrix}CH_3.C{=}N\\ |\\ HC{=}C\end{matrix}\begin{matrix}>N.C_6H_5\\ \\ \diagdown O.C_2H_5\end{matrix} + H_2O,$$

forming thus (1)phenyl(3)methyl(5)ethoxypyrazol.

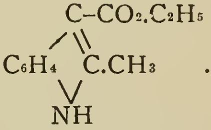
Entirely analogous results were obtained in the case of oxalacetic-ether hydrazide,



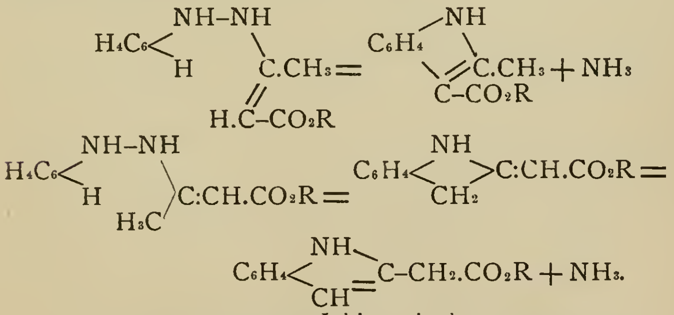
$$\begin{matrix}CO_2.C_2H_5.C.NH.NH.C_6H_5\\ \|\\ H.C.CO_2.C_2H_5\end{matrix}$$

, except that here the conversion into an indol derivative (case *b*) has not yet been accomplished.

Ethylic α-methylindol-β-carboxylate,



.—It is evident that acetacetic-ether hydrazide can lose ammonia (one molecule) in one of two ways:



(I)

(II)

Indol-α-acetic ether.

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[1] Ann. Chem. (Liebig) **266**, 124.

[2] *Ibid.* **266**, 73.

That this takes place exclusively according to reaction (I) was proved by the direct synthesis of ethylic α-methylindol-β-carboxylate: α-methylindol-β-carboxylic acid (melting-point found 176°) was made, according to Ciamician and Magnanini's[1] directions, from methylketol, and the acid converted into the silver salt. As the free acid loses carbon dioxide very readily, the salt was prepared by adding silver nitrate to a neutral solution of the ammonium salt in the cold. The white, flocculent precipitate thus obtained was well washed, dried in a vacuum, and, after moistening with ether, heated for 10 hours on a water-bath with twice the calculated amount of ethyl iodide. The ethyl ester thus obtained crystallised in colorless needles, melting at 131°, and was identical in all its properties with Nef's indol derivative.[2] I prepared the latter in large amounts according to Nef's directions, and obtained about a 30-per cent. yield. The crude product crystallises from alcohol, at first in scales, but, after repeated crystallisation, is obtained in lustreless needles. The melting-point is 131° and not 134°. The substance gives no coloration with ferric chloride. It is remarkably stable towards alcoholic potash, and can be heated for a day with a large excess without much change. If heated in a sealed tube, however, at 150° for 6 hours with twice the calculated amount of caustic potash, it is split quantitatively into methylketol and potassic carbonate. The ease with which the carboxyl group is split off here is noteworthy, because a number of indol derivatives, *e. g.* indol-α-carboxylic acid, have been obtained by melting indol homologues with caustic potash.[3] The methylketol formed was distilled over with steam, and obtained practically pure, melting at 56°–60° and showing all the characteristic reactions of this substance.[4] For the analysis it was recrystallised from ligroin (melting-point found 60°).

0.1817 gram substance gave 0.5462 gram CO_2 and 0.1150 gram H_2O.

0.2112 gram substance gave 20.1 cc. moist nitrogen at 25° and 746 mm.

	Theory for C_9H_9N.	Found.
C	82.44	81.99
H	6.86	7.03
N	10.69	10.70

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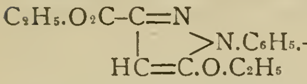
[1] Ber. d. chem. Ges. **21**, 1925.

[2] Ann. Chem. (Liebig) **266**, 73.

[3] Ciamician and Zatti: Ber. d. chem. Ges. **21**, 1938.

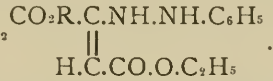
[4] Jackson: *ibid.* **14**, 879; Fischer: Ann. Chem. (Liebig) **236**, 127.

Ethylic (1)*phenyl*(5)*ethoxypyrazol*(3)*carboxylate*,



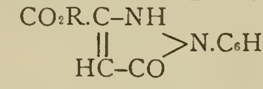
$$\begin{array}{l} C_2H_5.O_2C\text{–}C{=}N \\ \qquad\quad | \qquad > N.C_6H_5. \\ \qquad HC{=}C.O.C_2H_5 \end{array}$$

—Oxalacetic ether reacts with phenylhydrazine,[1] forming a substance which is to be regarded as oxalacetic-ether hydrazide,[2]



$$\begin{array}{l} CO_2R.C.NH.NH.C_6H_5 \\ \qquad\quad \| \\ \quad H.C.CO.O.C_2H_5 \end{array}$$

. This compound, as W. Wislicenus has shown, loses one molecule of alcohol very readily at higher temperatures, forming ethylic (1)phenyl(5)pyrazolon(3)carboxylate,



$$\begin{array}{l} CO_2R.C\text{–}NH \\ \qquad\quad \| \qquad > N.C_6H_5. \\ \qquad HC\text{–}CO \end{array}$$

It was expected that concentrated sulphuric acid would convert it, as analogous to the acetacetic-ether hydrazide, into ethylic indol-$\alpha\beta$-dicarboxylate, with elimination of one molecule of ammonia, but this is not the case.

The oxalacetic-ether hydrazide was prepared by adding phenylhydrazine to oxalacetic ether (one molecule), taking care that the temperature does not rise above 50°; after standing for 2 hours, ether was added, and the ethereal solution washed with dilute sulphuric acid, and then dried with calcic chloride. The ether was distilled off at low temperature, and the last traces removed over sulphuric acid in a vacuum. The yellowish solid left was well washed by decantation with ligroin (boiling-point 70°–80°), and so an almost pure white oxalacetic-ether hydrazide obtained, melting at 76°–78°.

The hydrazide, when treated with dehydrating agents, loses one molecule of water, forming a neutral body, melting at 83°–84°. In all cases, however, ethylic (1)phenyl(5)pyrazolon(3)carboxylate and the free acid are the chief products formed; and these, being both acid in nature, can easily be separated from the neutral compound, by extracting with ether and shaking with sodic hydroxide.

The following yield of the new substance was obtained:

(*a*) On treating with concentrated sulphuric acid at 0° and, after 10 minutes' standing, pouring on ice, and extracting with ether, etc.:

7.7 grams hydrazide gave 0.7 gram.
3.5 grams hydrazide gave 0.4 gram.

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[1] Ann. Chem. (Liebig) **246**, 319.

[2] *Ibid.* **266**, 65.

(*b*) On treating an alcoholic solution at 0° with dry hydrochloric acid, warming gently to 60°, and then pouring into water and extracting, etc.:

2 grams hydrazide gave 0.2 gram.

(*c*) same as (*b*), except that acetic acid was used instead of alcohol:

2 grams hydrazide gave 0.2 gram.
2 grams hydrazide gave 0.3 gram.

The best yield was finally obtained (5 grams from 20 grams hydrazide) by saturating an acetic-acid solution of the hydrazide at 0° with dry hydrogen chloride, and then warming on a water-bath at 60° for an hour, pouring into water, etc. The ethereal solutions were dried with calcic chloride, and the yellowish-colored solid left after removing the ether was recrystallised from dilute alcohol until colorless. It was obtained in needles, melting at 83°–84°, and, after drying over sulphuric acid in a vacuum, gave the following result on analysis:

I. 0.2048 gram substance gave 0.4836 gram CO_2 and 0.1200 gram H_2O.

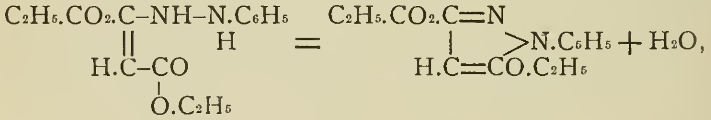
II. 0.3282 gram substance gave 0.7710 gram CO_2 and 0.1830 gram H_2O.

III. 0.3443 gram substance gave 34 cc. moist nitrogen at 18° and 757 mm.

IV. 0.1925 gram substance gave 18.4 cc. moist nitrogen at 20° and 755 mm.

	Theory for $C_{14}H_{16}N_2O_3$.	Found.			
		I.	II.	III.	IV.
C	64.61	64.40	64.07	...	...
H	6.15	6.51	6.19	...	...
N	10.77	...	...	11.23	10.80

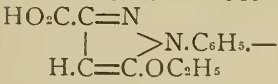
Oxalacetic-ether hydrazide, $C_{14}H_{18}N_2O_4$, has therefore lost one molecule of water; that the splitting off of water takes place thus:



$$\begin{array}{l} C_2H_5.CO_2.C{-}NH{-}N.C_6H_5 \\ \qquad\quad \| \qquad\qquad H \\ \quad H.C{-}CO \\ \qquad\qquad | \\ \qquad\qquad O.C_2H_5 \end{array} = \begin{array}{l} C_2H_5.CO_2.C{=}N \\ \qquad\quad | \qquad > N.C_6H_5 \\ \quad H.C{=}CO.C_2H_5 \end{array} + H_2O,$$

is proved by the further study of the resulting product. The new compound is very soluble in most organic solvents except ligroin; it is insoluble in water. It possesses weak basic properties, dissolving in concentrated acids, but on adding water the substance comes down unchanged. That it has an ethoxy group, as well as an ethylated carboxyl group, is proved by what follows.

(1)*Phenyl*(5)*ethoxypyrazol*(3)*carboxylic acid*,



$$\begin{array}{l} HO_2C.C{=}N \\ \quad | \qquad > N.C_6H_5 \\ H.C{=}C.OC_2H_5 \end{array}$$

.—The ester just described is heated on a water-bath for 8 hours with twice the calculated amount (the same result is obtained if 10 times this amount is used) of alcoholic potash. After driving off the alcohol and taking up with water, dilute hydrochloric acid precipitates a greyish-white substance. Recrystallised twice from much boiling water, it is obtained in transparent plates or in flat needles, which become opaque on drying at 110° and melt at 152°–153°.

I. 0.2022 gram substance, dried at 110°, gave 0.4578 gram CO_2 and 0.0982 gram H_2O.

II. 0.2174 gram substance gave 0.4979 gram CO_2 and 0.1058 gram H_2O.

III. 0.1928 gram substance gave 20.2 cc. moist nitrogen at 11° and 738 mm.

	Theory for $C_{12}H_{12}N_2O_3$.	Found.		
		I.	II.	III.
C	62.07	61.74	62.41	...
H	5.17	5.41	5.41	...
N	12.07	...	...	12.06

The acid is readily soluble in ether, chloroform, and alcohol; it dissolves with difficulty in boiling, and only very slightly in cold water. It gives no coloration with ferric chloride. A hydrochloride separates out in needles on dissolving the acid in a small amount of warm concentrated hydrochloric acid and cooling; it is decomposed by water. That the acid is monobasic is proved by the analysis of the barium and calcium salts.

Barium salt, $(C_{12}H_{11}N_2O_3)_2Ba.2H_2O$.—The barium salt was prepared by heating the acid with water and an excess of barium carbonate until neutral reaction sets in. After filtering and concentrating the salt crystallises out in colorless needles. The salt, after standing in a desiccator for 36 hours, lost two molecules of crystal-water on drying at 140°–150°.

0.9808 gram substance, dried 4 hours at 150°, lost 0.0292 gram H_2O.

	Theory.	Found.
H_2O	2.92	2.98

The analysis of the anhydrous salt gave the following result:

I. 0.2182 gram substance gave 0.3820 gram CO_2 and 0.0844 gram H_2O.

II. 0.2096 gram substance gave 0.0813 gram $BaSO_4$.

	Theory for $(C_{12}H_{11}N_2O_3)_2Ba$.	Found.	
		I.	II.
C	48.08	47.76	...
H	3.67	4.29	...
Ba	22.87	...	22.81

Calcium salt, $(C_{12}H_{11}N_2O_3)_2Ca.4H_2O$.—The calcium salt was prepared by a method entirely analogous to that for the barium salt. It is more soluble in water than the latter and crystallises in rhombic plates, containing four molecules of crystal-water.

0.2360 gram substance, air-dried (14 hours), lost 0.0284 gram H_2O on heating to constant weight at 110°.

	Theory.	Found.
H_2O	12.54	12.04

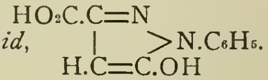
The anhydrous salt gave the following result on analysis:

I. 0.1638 gram substance gave 0.3441 gram CO_2 and 0.0680 gram H_2O.

II. 0.0980 gram substance gave 0.0253 gram $CaSO_4$.

	Theory for $(C_{12}H_{11}N_2O_3)_2Ca$.	Found.	
		I.	II.
C	57.37	57.29	...
H	4.38	4.61	...
Ca	7.97	...	7.57

(1)*Phenyl*(5)*oxypyrazol*(3)*carboxylic acid*,



$$\begin{array}{l} HO_2C.C{=}N \\ \quad\;\, | \qquad > N.C_6H_5. \\ H.C{=}C.OH \end{array}$$

The presence of an ethoxy group in the acid just described is proved by heating it (3 grams) in a sealed tube with 12 cc. concentrated hydrochloric acid at 150° for two hours. On opening the tube much ethyl chloride is liberated, as shown by its burning with green-tinged flame. The residue is diluted with water, the dark-brown mass filtered off, dissolved in sodic carbonate and reprecipitated by dilute hydrochloric acid. The substance was purified by repeated crystallisation from glacial acetic acid, and obtained in colorless needles, melting at 252°–253°.

0.1387 gram substance, dried at 110°, gave 0.2996 gram CO_2 and 0.0552 gram H_2O.

	Theory for $C_{10}H_6N_2O_3$.	Found.
C	58.82	58.90
H	3.92	4.42

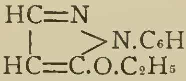
This acid can naturally be obtained in one operation from the ethylic (5)ethoxypyrazol(3)carboxylate by heating in sealed tubes at 150° for two hours. Longer heating is harmful in all cases owing to the instability of the resulting acid.

Phenyloxypyrazolcarboxylic acid is very difficultly soluble even in boiling water and separates out in needles on cooling. The aqueous solution gives a purplish-blue coloration with ferric chloride. The substance is far less stable than the corresponding ethoxy acid: it loses carbon dioxide on heating to 230°, and although very nearly one molecule is split off in this way, the residue consists in great part of charred matter and not a trace of (1)phenyl(5)oxypyrazol was obtained. In attempting to make the barium and the calcium salt of the acid as above in the case of the ethoxy acid, it was found that on concentrating the solutions, deep reddish-violet coloration and complete decomposition sets in; this is also true of the ammonium salt.

A silver salt was, however, obtained by adding silver nitrate in the cold to the carefully neutralised solution of the ammonium salt. The salt comes down as a colorless, gelatinous precipitate, and the analysis shows that two atoms of hydrogen have been replaced by silver.

0.2660 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2770 gram CO_2, 0.0446 gram H_2O and 0.1365 gram Ag.

	Theory for $C_{10}H_6N_2O_3Ag_2$.	Found.
C	28.70	28.40
H	1.43	1.86
Ag	51.63	51.32

(1)*Phenyl*(5)*ethoxypyrazol*, 

$$\begin{array}{l} HC{=}N \\ \mid \qquad > N.C_6H_5. \\ HC{=}C.O.C_2H_5 \end{array}$$

—(1)Phenyl(5)ethoxypyrazol(3)carboxylic acid, when heated to 205°, begins to lose carbon dioxide; one molecule is split off almost quantitatively, as shown by the following experiment:

10.71 grams substance, heated in a stream of dry air, first at 205° and then gradually up to 230°, lost 1.825 gram CO_2.

Theory for one molecule.	Found.
18.97	17.40

There is left a dark red-colored oil of weak basic properties. Attempts to distil it under reduced pressure showed that it does not boil without decomposition. It is not volatile with steam, and, if heated in a sealed tube with concentrated hydrochloric acid at 150°, is completely decomposed.

That the oil is phenylethoxypyrazol could, however, be proved by the isolation of a platinum double salt: the substance was dissolved in alcoholic hydrochloric acid, and the calculated amount of platinic chloride, dissolved in alcohol, added. After a short time the double salt begins to separate in yellow plates, which, recrystallised from alcoholic hydrochloric acid several times, are obtained in pale yellow needles melting at 141°–3°. For the analysis the salt was dried over sulphuric acid and lime in a vacuum.

I. 0.2654 gram substance gave 0.3243 gram CO_2 and 0.0998 gram H_2O.

II. 0.2981 gram substance gave 18.5 cc. moist nitrogen at 20° and 744 mm.

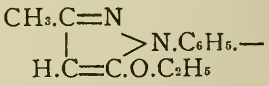
III. 0.2240 gram substance gave 0.0555 gram Pt.

IV. 0.2695 gram substance gave 0.2859 gram AgCl (Carius).

	Theory for $(C_{11}H_{12}N_2O, HCl)_2.PtCl_4$.	Found.			
		I.	II.	III.	IV.
C	33.65	33.33	...	...	...
H	3.31	4.17	...	...	...
N	7.14	...	6.92	...	...
Pt	24.78	...	...	24.78	...
Cl	27.04	...	...	...	26.24

THE THIRD CONDENSATION-PRODUCT OF ACETACETIC-ETHER HYDRAZIDE.

(1)*Phenyl*(3)*methyl*(5)*ethoxypyrazol*,



$$\begin{array}{l} CH_3.C{=}N \\ \;|\qquad\quad > N.C_6H_5.— \\ H.C{=}C.O.C_2H_5 \end{array}$$

Freer[1] has recently published a brief notice of a new compound obtained by treating acetacetic ether with phenylhydrazine hydrochloride. He gives this substance the formula $C_{10}H_{10}N_2O$ and supposes it may be an isomer of Knorr's phenylmethylpyrazolon. His conclusions are based entirely on conjectures and are without the slightest experimental basis, as the analysis of the product does not agree at all well with the formula assumed.

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[1] J. prakt. Chem. [2], 45, 414.

In view of the above results with oxalacetic-ether hydrazide, it seemed highly probable that Freer's product was formed from acetacetic-ether hydrazide by the splitting off of one molecule of water, and not of alcohol, as Freer assumes—$C_{12}H_{16}N_2O_2 = H_2O + C_{12}H_{14}N_2O$ (*cf.* page 577).

Freer's condensation-product was therefore made according to his directions in considerable quantity. The resemblance in its properties to those of ethoxyphenyl pyrazol, obtained above, is a very close one. The substance does not distil under reduced pressure entirely without decomposition, and this explains the poor analyses of Freer, which agree about as well for one as the other formula. It forms, however, a fine crystalline platinum double salt, which is best obtained by passing dry hydrochloric acid in excess into an ethereal solution of the oil, and then adding the calculated amount of platinic chloride dissolved in alcohol. After standing for a time, the double salt separates out in reddish-yellow plates which, recrystallised once from alcoholic hydrochloric acid, are obtained in yellow six-sided prisms, melting at 191°. For the analysis the salt was dried over sulphuric acid and lime in a vacuum.

I. 0.2515 gram substance gave 0.3274 gram CO_2 and 0.0906 gram H_2O.

II. 0.1976 gram substance gave 0.2567 gram CO_2 and 0.0717 gram H_2O.

III. 0.3594 gram substance gave 22.5 cc. moist nitrogen at 27° and 750 mm.

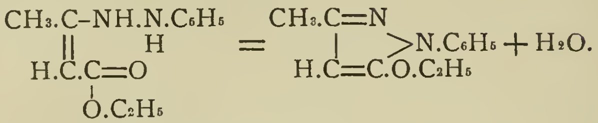
IV. 0.2656 gram substance gave 17 cc. moist nitrogen at 23° and 750 mm.

V. 0.2732 gram substance gave 0.0645 gram Pt.

VI. 0.2493 gram substance gave 0.2625 gram AgCl (Carius).

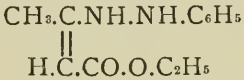
	Theory for $(C_{12}H_{14}N_2O,$ $HCl)_2.PtCl_4$.	Theory for Freer's $(C_{10}H_{10}N_2O,$ $HCl)_2.PtCl_4$.	Found.					
			I.	II.	III.	IV.	V.	VI.
C	35.44	31.70	35.50	35.43	...	...	...	...
H	3.69	2.91	4.02	4.03	...	...	...	...
N	6.89	7.39	...	...	6.78	7.07	...	...
Pt	23.92	25.63	...	...	...	...	23.61	...
Cl	26.10	28.14	...	...	...	...	...	25.91

The analyses agree so well with the formula $C_{12}H_{14}N_2O$ that there can be no doubt that in the above treatment acetacetic-ether hydrazide has lost one molecule of water, forming phenylmethyl ethoxypyrazol, as follows:



$$\begin{array}{l}CH_3.C{-}NH.N.C_6H_5\\ \quad \| \qquad\quad H\\ H.C.C{=}O\\ \qquad | \\ \qquad O.C_2H_5\end{array} = \begin{array}{l}CH_3.C{=}N\\ \quad | \qquad >N.C_6H_5\\ H.C{=}C.O.C_2H_5\end{array} + H_2O.$$

This has also been confirmed by the direct conversion of acetacetic-ether hydrazide into the above pyrazol derivative by means of alcohol containing a small amount of hydrochloric acid, in the cold.[1]

It is therefore a very noteworthy fact that the acetacetic-ether hydrazide,  $\begin{array}{l}CH_3.C.NH.NH.C_6H_5\\ \quad \|\\ H.C.CO.O.C_2H_5\end{array}$, according to the conditions employed, can lose one molecule of ammonia, water, or ethyl alcohol, forming an indol, a pyrazol or a pyrazolon derivative, respectively.

Worcester, Mass., *June*, 1892.

THE DECOMPOSITION OF SILVER CHLORACETATE CONSIDERED IN THE LIGHT OF OSTWALD'S THEORY OF AFFINITY.

By J. H. Kastle.

It has been a matter of common observation on the part of those who have investigated the halogen substitution-products of the fatty acids, that their salts are unstable, and that they readily decompose either spontaneously or by the aid of water, into the chloride of the metal and some acid derivative. This kind of decomposition has been made the subject of a special investigation by Beckurts and Otto,[2] and it is to their labors in this direction that we are principally indebted for our knowledge of these substances.

The present investigation was undertaken in the hope of being able, through a careful quantitative study of the decomposition of the silver salts of the halogen substitution-products of the fatty acids, to arrive at some general conclusion concerning the relative influence of the different halogens upon the decomposition, and to note the effect of the same halogen in different positions in the molecule, that is, to compare, for example, the rate of decomposition of α-brompropionate of silver with the same salt of the β-acid.

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[1] It follows from this that the product obtained by treating acetacetic-ether hydrazide with acetyl chloride [Ann. Chem. (Liebig) **266**, 76] is (1)phenyl(3)methyl(5)ethoxypyrazol. The acetyl chloride simply acts as a dehydrating agent, and this is undoubtedly the best method of obtaining this compound.—J. U. Nef.

[2] Ber. d. chem. Ges. **14**, 576.

With this end in view, a quantitative study was made of the rate of decomposition of silver chloracetate in the following way and with the following results.

The Rate of Decomposition of Silver Chloracetate.

This salt was prepared by neutralising silver carbonate with an aqueous solution of chloracetic acid, and in this way was obtained in needle-shaped crystals which, on analysis, gave numbers closely agreeing with the theory. The salt thus obtained was ground to a fine powder and carefully preserved in a tightly-stoppered bottle in the dark, under which conditions it undergoes but little alteration.

The conditions of the experiments were these:

0.2015 gram of the silver salt, or the thousandth of one equivalent in grams, was heated in a sealed glass tube in a bath, the temperature of which was kept constant at 134°–135° C., with 9 cc. of water, that is, with 500 times the quantity necessary for the complete decomposition of the weight of salt taken.

The sealed tubes were made as nearly as possible of the same size, that is, about six inches long. The bath was made of thin copper after the manner of a Carius furnace, the outer jacket of the bath being connected with a return-condenser and partially filled with xylene, the boiling of which served to keep the inner tube of the bath at the above-named temperature. After each experiment the sealed tube was at once removed from the bath and allowed to cool for 10 minutes, when it was opened and the amount of undecomposed silver salt determined by means of a standard solution of ammonium sulphocyanide.

I am aware that the conditions of these experiments may be improved upon, and that such as they are they are by no means easy to realise exactly in every instance; and hence I do not give these results as the very best attainable and free from all error, but simply as a fairly close approximation to the truth. The table below gives the results obtained and shows the rate per minute of this decomposition.

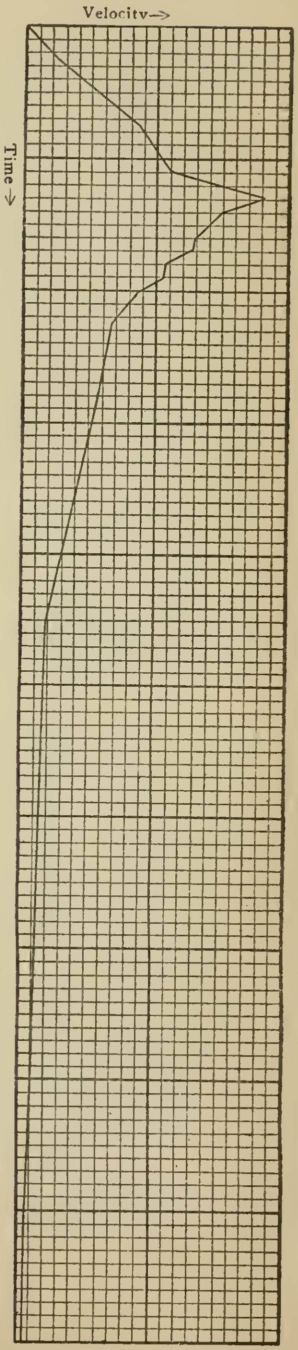
TABLE I.—*Decomposition of the Silver Chloracetate at* 135° *C.*

No. of Exp.	Substances taken.	Time in Bath at 135° C.	Percentage of Decomposition.	ϑ.
1	0.2015 gram silver chloracetate. 9 cc. of water.	5 min.	11.38	2.27
2	“ “	10	48.92	8.54
3	“ “	12	60.16	11.00
4	“ “	13	67.36	18.07
5	“ “	15	77.04	14.79
6	“ “	16	80.	12.96
7	“ “	17	82.60	13.
8	“ “	18	84.45	10.63
9	“ “	19	86.10	10.61
10	“ “	20	87.3	8.62
11	“ “	25	91.5	6.67
12	“ “	30	94.	5.88
13	“ “	60	97.24	1.8
14	“ “	120	97.97	0.44

In the last column, marked ϑ, are placed the numbers showing the average rate of speed of the decomposition at the several intervals of time. These numbers were arrived at in this way.

In Exp. No. 1 there was decomposed 11.38 per cent. of salt; hence the average rate of decomposition during the first five minutes is 2.27 per cent. per minute. In Exp. No. 2 there must have been decomposed at the end of the first five minutes as much as in Exp. No. 1, that is, 11.38 per cent., and hence there was left undecomposed at the end of the first five minutes 88.62 per cent. of the silver salt. In Exp. 2, however, there was decomposed altogether 48.92 per cent., hence during the second five minutes of this experiment there was decomposed $48.92 - 11.38 = 37.54$ per cent. $88.62 : 37.54 :: 100 : x$. $x = 42.36$ per cent.

This number 42.36 represents then the actual percentage of salt decomposed during the last five minutes of the second experiment as calculated upon the amount of undecomposed substance at the beginning of the second five minutes, and this divided by five gives the number representing the average rate of decomposition during the second five minutes. The numbers in the column ϑ if used as ordinates in the construction of a curve in which the different increments of time are projected on the axis of abscissæ, give a curve which, in spite of several slight irregularities, illustrates very clearly the decomposition of silver chloracetate under the above-mentioned conditions.



A study of this curve shows that the decomposition rises rapidly to a maximum, which it reaches even before the temperature of the solution has reached the highest attainable temperature of the bath, which is 135°, and which is not reached until twenty minutes after the tube is introduced. Having reached this maximum, the decomposition proceeds more and more slowly in spite of the fact that at the end of twenty minutes the bath and its contents have reached the highest attainable temperature under the given conditions; and finally at the end of three hours the decomposition is almost if not entirely complete.

That the change which here takes place is not a reversible one was shown by heating together a known quantity of freshly precipitated silver chloride and an equivalent quantity of glycollic acid under such conditions as were stated above. Under these circumstances no trace of silver could be detected in the solution, thus proving conclusively that the reaction here studied is not, for these conditions at any rate, a reversible one. Such being the case it was thought that the retardation of the velocity of the change might nevertheless be caused by the presence and action of glycollic acid, which is one of the products of the decomposition, and in order to settle this point the following experiment was tried:

0.0760 gram of glycollic acid together with 0.2015 gram of silver chloracetate and 9 cc. of water were heated in the bath at 135° C. for 15 minutes. The amount of decomposition was found to be 75.27 per cent.

Comparing this with the amount of decomposition in Exp. 5, Table I, which is 77.04 per cent., it will be seen that the difference is exceedingly small, and hence the retarding effect of the glycollic acid is but slight, and can scarcely be looked upon as sufficient to account for the great retardation which the curve on p. 589 indicates. If this reaction then is a non-reversible one—and such it has been shown to be—and if the soluble product of the decomposition, glycollic acid, does not exert any very considerable influence on the velocity of the decomposition, then plainly we must look to the quantity of water present at the different times as furnishing the only explanation of the curve expressing the velocity of the change. As a matter of fact it has already been noticed by Beckurts and Otto that this decomposition is much accelerated when the quantity of water present is small; but as these observers were chiefly engaged in studying this kind of decomposition with reference to the end-products of the reaction, it is not surprising that they should have contented themselves with merely a passing notice of this remarkable fact.

In order to make sure that the retardation of the velocity of this decomposition was due largely to an ever-increasing quantity of water, a number of experiments were made, the conditions and results of which are given below in Table II.

TABLE II.—*Showing the Effect of Water on the Decomposition of Silver Chloracetate.*

No. of Exp.	Quantity of Silver Salt taken.	Quantity of Water.[1]	γ.	Time.	Temperature.	Amount of Decomposition.
1	0.2015 gram.	1.8 cc.	100	1 hour.	100° C.	69.1 per cent.
2	"	3.6	200	"	"	60.1
3	"	5.4	300	"	"	52.
4	"	7.2	400	"	"	47.28
5	"	9.	500	"	"	43.36
6	"	18.	1000	"	"	31.13
7	"	27.	1500	"	"	23.70
8	"	36.	2000	"	"	21.
9	"	54.	3000	"	"	17.02
10	"	90.	5000	"	"	12.48
11	"	180.	10,000	"	"	8.30
12	"	360.	20,000	"	"	5.95
13	"	540.	30,000	"	"	3.10

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[1] The quantity of water which actually enters into reaction with the quantity of silver salt used in each of these experiments is 0.0180 gram.

In this table, in the column marked γ, are given numbers which represent the several quantities of water taken, in terms of the quantity necessary to secure the complete decomposition of the quantity of salt used as unity. In Exp. 5, for example, 500 in column γ signifies that the quantity of water actually employed, that is 9 cc., is 500 times the quantity necessary completely to decompose 0.2015 gram of the silver salt, $500 \times 0.0180 = 9$.

The results obtained in this last series of experiments show beyond a doubt that the quantity of water exerts a very marked and regular influence upon the course of this reaction; and they likewise enable one to account for the results obtained in the first series of experiments, and to interpret the curve on p. 589 as follows: When a tube containing 0.2015 gram of silver chloracetate and 9 cc. of water is introduced into the bath whose temperature is 134°–135° C., we may safely assume that the decomposition begins almost immediately, for the reason that the temperature of the bath under these circumstances never falls below 100° C., and at this temperature the decomposition proceeds fairly rapidly. At the beginning of the experiment we have 500 times the quantity of water necessary to insure the complete decomposition of the salt; and, as the temperature of the bath gradually rises, the decomposition proceeds with increasing velocity. Nevertheless, as more and more and more of the salt is decomposed, so larger and larger (proportionately) becomes the excess of water, so that after the maximum is reached, the curve, notwithstanding the fact that the temperature is constantly becoming higher, begins a gradual descent, because of the retarding effect of the increasing quantities of water. In order to determine more fully the influence of the glycollic acid upon the course of the reaction, the following experiments were tried, the results and conditions of which are indicated in Table III. In column VI of this table are also given, for the sake of comparison, the results before indicated in Table II.

It will be seen from this that the general effect of the glycollic acid is one of retardation; but a careful study of any of the results thus obtained—as was the case also with that obtained at 135° C. and cited above—reveals the fact that the retarding influence thus exerted is by no means sufficient to account for the great retardation experienced on dilution with water.

TABLE III.—*Showing the Effect of Glycollic Acid on the Decomposition of Silver Chloracetate.*

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
No. of Experiment.	Silver Salt Taken.	Quantity of Water.	Quantity of Glycollic Acid.	Percentage Amount of Decomposition.	Taken from Table II.	Retardation by Glycollic Acid.	Remarks.
1	0.2015 gr.	1.8 cc.	0.076 gr.	62.2	69.1	6.9	Time = 1 hr.
2	"	3.6	"	49.34	60.1	10.76	Temp. = 100° C.
3	"	5.4	"	43.95	52.	8.05	
4	"	7.2	"	41.86	47.28	5.42	
5	"	9.	"	38.9	43.36	4.46	
6	"	18.	"	27.25	31.13	3.88	
7	"	27.	"	20.82	23.70	2.88	
8	"	36.	"	18.61	21.00	2.39	
9	"	54.	"	12.55	17.02	4.47	
10	"	90.	"	8.33	12.48	3.65	
11	"	180.	"	5.44	8.30	2.86	
12	"	360.	"	3.35	5.95	2.60	
13	"	540.	"	0.89	3.10	2.21	

For the sake of illustration, the consideration of two of the experiments upon this point will suffice: In Exp. 1, Table III, we find that when 0.2015 gram of silver chloracetate is heated with 1.8 cc. of water at 100° C. for one hour, 69.1 per cent. of the salt is decomposed; whereas, in Exp. 10, the conditions being the same except that here 90 cc. of water are used, we find only 12.48 per cent. of the salt decomposed. In no case now does the full equivalent of glycollic acid produce a retardation greater than 10.76 per cent. (see column VII, Table III), the average being much less. Inasmuch as the glycollic acid formed in Exp. 10 as the result of the decomposition is only about one-eighth of the quantity used in the experiments tried for the purpose of discovering its effect, it follows that the retardation in this particular case due to the glycollic acid could hardly be greater than 2 per cent. Owing to the difference in the quantities of water employed in these two experiments 1 and 10, however, we find a retardation of 56.62 per cent., or 54.62 per cent. above that which could have been brought about by the glycollic acid. Again, a comparison of the results of Experiments 1 and 10 in columns V and VI, Table III—the conditions of which were exactly the same except that in those of column V one equivalent, 0.076 gram of glycollic acid was introduced—shows the retardation produced by the same quantity of water to be in each case nearly the same, being in the one 53.37 per cent. and in the other 56.62 per cent. In fact it may be said that the results given in these two columns V and VI illustrate equally well, and in most instances to almost exactly the same degree, the retarding effect of water upon the course of the reaction.

The decomposition of silver chloracetate in the presence of water into glycollic acid and silver chloride is a clean one and, so far as I have been able to discover, unattended by the formation of secondary products of any kind; and, furthermore, the silver chloride exerts no influence upon the rate of the decomposition, as is shown by the following experiments:

I. 0.2015 gram silver chloracetate and 0.1435 gram silver chloride—an equivalent quantity—heated with 36 cc. water at 100° C. for 1 hour, gave 21.1 per cent. decomposed.

II. Conditions, substances and quantities same as I gave 20.8 per cent. decomposed.

Comparing these results with that of Experiment 8, Table II, which is 21 per cent., we see that the silver chloride exerts no influence upon the rapidity of the change.

The retarding influence of water on the velocity of the decomposition, and it being, moreover, the substance which *apparently* produces the change and which certainly does enter into reaction with the other substances involved, shows that this reaction, in spite of its simplicity, is anomalous.

For these facts, remarkable as they are, no explanation has ever been offered, so far as I know. As stated above, Beckurts and Otto were the first to note that the decomposition of silver chloracetate proceeds more rapidly in a small than in a large quantity of water; they offer no explanation of the fact, however, and in all of their papers upon this and closely related subjects which have come under my notice—and there are several—nothing has been found by way of explanation or of theoretical significance beyond a brief statement concerning certain experiments with dichloracetic acid, the import of which is that the rapidity of the decomposition of the silver salt of this acid depends upon a destruction of the equilibrium due to the insolubility of silver chloride, and not *solely* upon the affinity of the metal for the halogen.[1]

While this is doubtless true, and applicable perhaps to the decomposition of the silver salt of monochloracetic acid as well, this explanation is not sufficiently far-reaching, and the only explanation of the facts above stated which seems at all plausible and worthy of consideration is that furnished by Ostwald's studies on the affinity of acids. According to this distinguished investigator, the strength or, better perhaps, the affinity of any acid depends upon the extent to which it is dissociated into its ions, and all acids would have equal affinities if fully dissociated.[1] He has proved experimentally that weak acids become rapidly stronger as the dilution increases. and believes the cause of this to be that such acids are but little dissociated in their concentrated state or at moderate dilution: dissociation, increasing with the dilution, greatly increases the affinity of these acids. Strong acids, on the other hand, like hydrochloric, which are already tolerably far dissociated in their concentrated state, and at moderate dilutions, do not gain much in strength by further dilution. For the sake of clearness regarding the effect of dilution upon the relative affinities of strong and weak acids a few selections have been made from Ostwald's tables and are given below in Table IV.

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[1] Ber. d. chem. Ges. **14**, 582.

TABLE IV.—*Relative Affinities of Acids at Different Dilutions.*

Name of Acid.	Strength of Solution.		
	Normal.	$\frac{1}{3}$ Normal.	$\frac{1}{10}$ Normal.
Nitric,	1.00	1.00	1.00
Hydrochloric,	.90	.98	.979
Chloric,	.932	...	.998
Acetic,	.0094	.0123	.0735
Monochloracetic,	.046	.070	.213
Dichloracetic,	.165	.33	.488

It will be seen that further dilution does not increase the affinity of strong acids which are moderately dilute. Hydrochloric acid, for example, is increased only .08 in passing from a normal to a $\frac{1}{3}$-normal state of dilution, or becomes only about one-eleventh stronger, and having reached this strength it is not increased at all in passing to a $\frac{1}{10}$-normal state of dilution. Monochloracetic acid, on the other hand, which is a weak acid, rapidly increases in strength as it is diluted, being in $\frac{1}{10}$-normal solution about five times as strong as it is in the normal. In the light of this theory of affinity, then, the decomposition of silver chloracetate in the presence of water, and the retardation of the change produced by the excess of water, may be explained in this way: we have in the compound, silver chloracetate, $CH_2Cl.COOAg$, two acids, one hydrochloric, the other chloracetic, exerting their affinity on one metal, silver.

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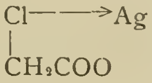
[1] Outlines of General Chemistry. By W. Ostwald. Translated by James Walker. p. 361.

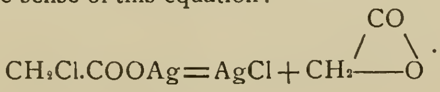
This may be expressed graphically by the aid of these two formulas:



$$\begin{array}{l} Cl \longrightarrow Ag \\ | \\ CH_2COO \end{array} \quad \text{and} \quad (CH_2ClCOO) \rightarrow Ag.$$

The one of these two acids, hydrochloric, is one of the strongest acids known, and, according to Ostwald, its strength will not be greatly increased by dilution with water, in fact it will not be increased at all appreciably after the state of moderate dilution is passed.

It will be seen from the above table, for example, after converting the numbers there given into whole numbers by multiplying by 100, that the relative affinity of this acid is 90 in normal solutions, 98 in $\frac{1}{3}$-normal, and essentially the same in $\frac{1}{10}$-normal, that is 97.9. Chloracetic, on the other hand, is a weak acid, capable, however, of showing a greater and greater affinity as it is diluted. In normal solutions, for example, its relative affinity is 4.6; in $\frac{1}{3}$-normal it is 7, or nearly twice as strong; and in $\frac{1}{10}$-normal it is 21.3, or nearly 5 times as strong as it is in the normal state of dilution. Hence we may imagine it to become through dilution as fully dissociated, and hence as strong, as hydrochloric acid itself. The facts are, with reference to the decomposition of chloracetate of silver, a salt in which both of these acids—the one potentially, the other actually—are exerting their affinity upon the silver, that the decomposition of this substance, in the dry state, and in that in which both of these acids, so to speak, are in a highly concentrated form, and therefore the one very strong and the other very weak, is one of an explosive kind, that is, the affinity of the hydrochloric acid so far exceeds that of the monochloracetic acid as to break down the molecule, the decomposition taking place as rapidly as possible in the sense of this equation:



$$CH_2Cl.COOAg = AgCl + CH_2\begin{array}{c} \quad CO \\ \diagup \quad \diagdown \\ \text{———}O \end{array}.$$

When the silver chloracetate is mixed with a small quantity of water—as it is in Exp. 1, Table II, for example, where it is in nearly ½-normal solution—the affinity of the hydrochloric acid probably becomes as great as 95, or one-eighteenth stronger; on the other hand, the affinity of the chloracetic acid probably becomes 6, or about one-fourth stronger. Although the hydrochloric acid is still stronger and much stronger, nevertheless the balance of the increase in strength is in favor of the chloracetic acid, and hence the decomposition, while taking place rapidly, does not begin to compare in rapidity with that which takes place in the dry state, or with just a drop or two of water: in other words, the presence of even a comparatively small quantity of water, by virtue of its more greatly increasing the strength of the chloracetic than of the hydrochloric, has retarded the action to a considerable extent.

In the light of this hypothesis, the results obtained in the several series of experiments are no longer difficult to explain: the regular retardation of the velocity of the change as shown in Table II is accounted for on the assumption that the affinity of the hydrochloric acid soon becomes a constant force, and one which is sufficient to disintegrate the molecule in question; and that opposing this constant force is another, that of the affinity of chloracetic acid, which, while much weaker than the former at the start, rapidly increases in strength in consequence of dilution, until at last it becomes almost, if not quite, powerful enough to hold it, the former, completely in check, and chemical equilibrium is the result.

I am not unaware that there may be, and doubtless are, other elements in this problem than those which are here discussed; nor unmindful that the experimental difficulties in the way of an ultimate solution of it are many; nevertheless this hypothesis opens up an interesting field of inquiry and research, and is important not only in its immediate application, but also in its more remote, though direct, bearing upon Ostwald's theory of affinity as well.

Work is now in progress, the purpose of which is to test this hypothesis with regard to the decomposition of other salts of this acid, and likewise the various salts of bromacetic and other closely related acids. It may be said in this connection that already sufficient experimental data are at hand concerning the decomposition of potassium chloracetate to indicate that its decomposition in water, like that of the corresponding silver salt above discussed, suffers a gradual retardation with increasing quantities of the solvent.

This is all the more interesting in consequence of the fact that potassium chloride is so easily soluble in water, and hence does not disturb the reaction by being removed from the field in consequence of precipitation, as is the case with the silver salt. The effect of the glycollic acid upon the change will also, in this case, be exhaustively studied in the hope of being able to define more exactly the influence which it exerts upon the speed of such decompositions; and in consequence of the greater possibilities presented by this potassium salt, it is hoped to arrive ultimately at a full and complete explanation of the mechanism of this interesting phase of chemical action.

In conclusion I desire to thank Mr. B. C. Keiser for his excellent assistance in the experimental part of this investigation.

A. AND M. COLLEGE OF KENTUCKY, LEXINGTON, *June*, 1892.

ON THE PREPARATION AND CONSTITUTION OF PARA-ANTHRACENE.

BY C. E. LINEBARGER.

The action of sunlight upon solutions of anthracene was first observed and studied by Fritzsche,[1] who describes the geometrical form of the crystals thus obtained from alcoholic and benzene ("Steinkohlenöl") solutions. Graebe and Liebermann,[2] in their work on alizarine, also prepared the substance, without making, however, any considerable study of it. Schmidt,[3] in investigating the action of nitric acid on anthracene, also occupied himself with a study of the behavior of para-anthracene towards nitric acid. Recently Elbs[4] has determined the solubility of para-anthracene in various solvents, and cryoscopically its molecular mass. This he found to be double that of anthracene, viz. $(C_{14}H_{10})_2$.

The method generally employed in the preparation of para-anthracene consists in exposing a solution of anthracene in benzene[5] to the direct action of the sun's rays. The almost insoluble para-anthracene separates out in the form of minute white crystals which adhere so firmly to the sides of the vessel in which the solution is contained that they cannot be entirely removed by mechanical means. This crystalline crust shuts out much light and thus retards the speed of transformation. Thinking that this phenomenon might not occur if other solvents were used, I prepared saturated solutions of anthracene[1] in dry chloroform and in dry carbon bisulphide.[2]

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[1] J. prakt. Chem. **101**, 337.

[2] Ann. Chem. (Liebig) Supl. **7**, 264.

[3] J. prakt. Chem. [2] **9**, 248.

[4] Ibid. [2] **44**, 467.

[5] Fritzsche (*loc. cit.*) employed alcohol also.

After an exposure of a few days, white glancing crystals appeared floating about on the surface of the chloroformic solution, which had turned almost black. When no more crystals seemed to separate out, most of the chloroform was distilled off, and the dark-colored residue filtered and washed with cold acetic ether. A perfectly white crystalline mass was thus obtained, melting well at 243°, and is therefore para-anthracene. No difficulty was experienced from the crystals sticking to the sides of the vessel, as in the case of benzene solution.

The solution of anthracene in carbon bisulphide also turned black after a few days of exposure, but no separation of crystals took place. The carbon bisulphide was distilled off, and the black residue, in which could be seen many small glistening tablets similar to those of anthracene, was washed with cold acetic ether until the washings were not colored. The resulting grayish-white mass melted at 208°–210°, *i. e.* the melting-point of anthracene. Para-anthracene is, then, not formed from anthracene in carbon-bisulphide solution. This shows that the solvent has a certain effect upon the formation of para-anthracene from anthracene, and that the transformation does not take place in every solvent employed.

The experiments of Beckmann[3] show that the nature of the solvent has considerable influence upon the size of the molecules of the dissolved substance.

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[1] The pure hydrocarbon was prepared as follows: Ordinary green anthracene, containing about 60 per cent. of the pure hydrocarbon, was heated with reflux condenser for 24 hours with about twice its volume of acetic ether. The dark-colored solution was filtered off, and the residue washed with cold acetic ether until the washings passed through colorless. The light green product was subjected to sublimation, the process being accelerated by passing a rapid current of air over the melted anthracene contained in a retort. By a second sublimation, quite pure anthracene was obtained.

[2] Carbon bisulphide was hardly a suitable solvent, as it is itself decomposed by sunlight. Yet this decomposition takes place so slowly that it was at first thought that that circumstance would have but little effect upon the transformation of anthracene into para-anthracene.

[3] Ztschr. phys. Chem. **6**, 437.

Compounds dissolved in the alcohols, phenols, ethers, etc., generally have a normal molecular mass, while when dissolved in benzene, carbon bisulphide, chloroform, ethylene bromide, etc., they have a tendency to form more complex, especially double, molecules. It is not admissible to give as the reason of the non-transformation of anthracene into para-anthracene in carbon bisulphide solution, that the anthracene exists in solution as a double molecule, although such a view of the case is quite in accordance with a hypothesis (to be given below) which I have made in regard to the constitution of para-anthracene; for Beckmann[1] has shown that anthracene has a normal molecular mass when dissolved in carbon bisulphide. The matter was deemed of sufficient importance to warrant the investigation of the behavior of anthracene dissolved in a variety of solvents towards sunlight. As anthracene is not very soluble in most liquids, in order to reduce the quantity of solvent the samples were prepared as follows: Somewhat more anthracene than could be dissolved was added to each of the solvents; as soon as the anthracene changed into para-anthracene, a fresh portion of the former hydrocarbon entered into solution. Thus with a small quantity of the solvent a comparatively large quantity of anthracene could be transformed into para-anthracene.

The solutions were exposed about two months (summer of 1892). The precipitates of para-anthracene were then filtered off, washed with a little of the pure solvent, dried, and their physical properties noted. These are here given as briefly as possible, the examination of the crystals being done, of course, with the aid of a microscope.

Anthracene[2] dissolved in—

1. *Benzene*, colorless solution, six-sided prisms, m. p. 243°–244°.
2. *Toluene*, colorless solution, rhombic tablets, m. p. 244°.
3. *Xylene* (Kahlbaum's *puriss.*), colorless solution, rhombic tablets, exceptionally numerous and well formed, m. p. 244°.
4. *Ethyl benzene*, colorless solution, comparatively large elongated hexagonal plates, m. p. 244°.

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[1] *Loc. cit.*, p. 447.

[2] The anthracene employed in these experiments was prepared from anthraquinone by reduction with ammonia and zinc dust, and had been crystallised from alcohol until it possessed the bluish fluorescence characteristic of the pure substance.

5. *Alcohol* (99 per cent.), light-yellow solution, well defined rhombs, with an occasional hexagonal plate, m. p. 244°.

6. *Acetic acid* (glacial), light-yellow solution, poorly crystallised, only a few well defined rhombs present, m. p. 243°–245°.

7. *Ethyl benzoate*, light-yellow solution, six-sided plates, m. p. 244°.

8. *Benzene bromide*, solution yellow, hexagons few in number, m. p. 244°.

9. *Chloroform*, solution quite black, rhombic plates, not well crystallised, m. p. 244°.

10. *Ethylene bromide*, solution almost black, grayish-white plates similar to those of anthracene, green coloration with concentrated sulphuric acid, m. p. 210°–212°.

11. *Carbon bisulphide*, black solution, indefinitely crystallised, m. p. 207°–211°, green coloration with concentrated sulphuric acid.

The above experiments show that in the transformation of anthracene into para-anthracene, the solvent not only has influence upon the product, but is itself changed in some instances. The hydrocarbons of the benzene series remain unaltered, but all the solvents containing oxygen, although of various chemical constitutions, take on a light-yellow color, which indicates that some chemical change has probably taken place. This color does not deepen, even if the solution be exposed for a long time (four months) to sunlight, when once all the anthracene has been transformed into para-anthracene, showing that the change of color takes place only during the actual transformation of the anthracene into its polymer. The shade of yellow of all the solutions was about the same.

One other solvent besides carbon bisulphide was found not to permit of the transformation of the anthracene, viz. ethylene bromide. This is undoubtedly due to the fact that ethylene bromide, when exposed to the sun's rays, is itself decomposed into a brown, amorphous substance, adhering firmly to the glass, while the liquid assumes a dark-brown color. The decomposition does not proceed so rapidly as in the case of carbon bisulphide.

The non-transformation of anthracene into para-anthracene in carbon bisulphide and in ethylene bromide solution cannot be owing to the blackening of the solution and consequent exclusion of the light, for in chloroform solution, which turns black as rapidly as carbon bisulphide, the change takes place quickly; nor can it be owing to the presence of the halogens (bromine) in the molecule of the solvent, for the transformation is effected in benzene bromide with but slight change of color. Neither chloroform nor benzene bromide is decomposed by the direct action of the sun's rays; hence the non-transformation of anthracene into para-anthracene when dissolved in carbon bisulphide or ethylene bromide must be on account of the decompositions of the solvents. What the products of these decompositions are it is difficult to say, as they are black, amorphous masses easily undergoing alteration.

Of all the solvents used, xylene proved itself the best adapted for the preparation of para-anthracene. If a bottle nearly full of xylene to which nearly the equal weight of anthracene has been added, be exposed to sunlight, in a little while (depending of course upon the amount of sunshine) all the solid hydrocarbon will have been changed into its polymer, which can easily be separated from the last traces of anthracene by washing with hot benzene.

As stated above, para-anthracene has a molecular mass double that of anthracene, $C_{14}H_{10}$. The question arises, in what way do two molecules of anthracene unite to form one molecule of para-anthracene? So far as I know, no answer has been given to the question; accordingly the following is offered.

It is pretty well established that in anthracene, the so-called γ-carbon atoms have one bond in common, *i. e.* anthracene may be regarded as ethane in which four of the hydrogen atoms are replaced by two bivalent radicles, viz. phenylene; or, what amounts to the same thing, anthracene consists of three benzene rings, of which the middle one has two of its carbon atoms, in the para-position, bound directly together. This double linkage of the γ-carbon is quite loose, as shown by the ready oxidation of anthracene into anthraquinone, and the formation of addition-products with chlorine and bromine at low temperatures. It might be now that by the action of the sun's rays these double bonds would be set free in some way. If, then, a molecule of anthracene with its double bonds thus loosed should come within the sphere of action of another molecule in a similar condition, the free bonds of the one molecule might unite with the free bonds of the other, doubling up and forming a new molecule stable so far as the action of light is concerned. In direct sunlight, the equilibrium of the anthracene molecule is labile, while that of the para-anthracene is stable. On the other hand, under the influence of heat the para-anthracene molecule is in labile, and the anthracene in stable equilibrium, for at 244° the double molecule decomposes into two simple ones—para-anthracene changes into anthracene.

There is then in para-anthracene a ring of four carbon atoms, occupying with respect to the anthracene molecule the γ-position. No addition- or substitution-products of this ring have as yet been obtained, although it might be possible by means of the Friedel-Crafts reaction in carbon bisulphide solution to effect the substitution of bromine for hydrogen.

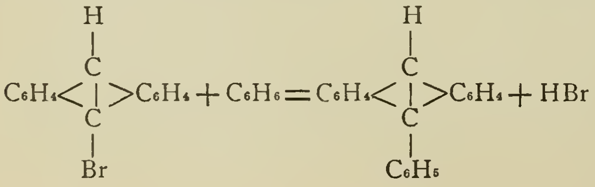
It is my intention to carry out some experiments with that end in view, as well as to determine what kind of light is most effective in transforming anthracene into para-anthracene.

CHICAGO, *September*, 1892.

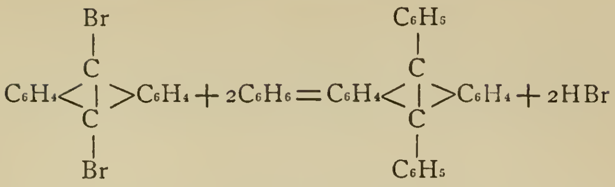
ON THE APPLICATION OF THE FRIEDEL-CRAFTS REACTION TO SYNTHESES IN THE ANTHRACENE SERIES.

BY C. E. LINEBARGER.

This paper contains an account of some experiments carried out with a view to effecting syntheses in the anthracene series by means of the action of aluminium chloride upon the γ-halogen (Cl, Br) substitution-products of anthracene in benzene solution. Although but negative results were obtained, they are of sufficient importance to merit publication and may serve to prevent others from working over the same ground. Theoretically, it is not impossible to obtain the phenylanthracenes by the application of the Friedel-Crafts reaction, according to the equations:



$$C_6H_4 \left< \begin{matrix} H \\ | \\ C \\ | \\ C \\ | \\ Br \end{matrix} \right> C_6H_4 + C_6H_6 = C_6H_4 \left< \begin{matrix} H \\ | \\ C \\ | \\ C \\ | \\ C_6H_5 \end{matrix} \right> C_6H_4 + HBr \qquad (I)$$



$$C_6H_4 < \begin{array}{c} Br \\ | \\ C \\ | \\ C \\ | \\ Br \end{array} > C_6H_4 + 2C_6H_6 = C_6H_4 < \begin{array}{c} C_6H_5 \\ | \\ C \\ | \\ C \\ | \\ C_6H_5 \end{array} > C_6H_4 + 2HBr \qquad (II)$$

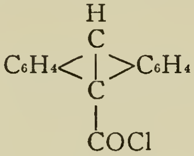
The following is a statement of my attempts to realise the above equations given as briefly as is consistent with clearness.

20 grams of powdered aluminium chloride were added to a solution of 20 grams of anthracene monobromide in 150 grams of benzene. At the ordinary temperature no reaction took place, but at about 50° C. hydrobromine acid commenced to pass off, and the reaction proceeded quite briskly at 60° to 70° C. When the evolution of gas slackened a little, I heated to boiling for a few minutes. The amount of hydrobromic acid given off corresponded to the theoretical quantity calculated according to equation (I). The product of the reaction, when cool, was treated with water in the usual way. The benzene solution was then separated from the water, dried over calcium chloride and distilled without a thermometer. After the benzene had been driven over, a reddish-brown distillate was obtained with high melting-point. This distillate was treated with hot alcohol and the solution filtered. Small, glistening scales just like those of anthracene separated out from the solution when it became cold. These crystals melted at 207° to 210° C. and gave the characteristic green color with concentrated sulphuric acid. About 5 grams of this crystalline product, which was undoubtedly anthracene, were obtained. Not a trace of phenylanthracene could be found. I repeated this experiment several times with varying quantities of aluminium chloride, benzene and monobromanthracene, but always obtained about the same results.

I went through similar experiments with dibromanthracene, benzene and chloride of aluminium, but never succeeded in obtaining any crystallisable compounds other than anthracene, although a considerable amount of resin was formed, which was very soluble in benzene. The reaction did not begin below the boiling-point of benzene, and then proceeded rapidly, the theoretical amount of hydrobromic acid, calculated according to equation (II), being given off.

In one experiment I employed dichloranthracene, but obtained the same products as with anthracene dibromide.

Graebe[1] has found that by heating anthracene and phosgene together in a sealed tube, a compound having the formula



$$C_6H_4 < \begin{array}{c} H \\ C \\ | \\ C \\ | \\ COCl \end{array} > C_6H_4$$

is formed. I tried to obtain the same substance by letting chloride of aluminium react with anthracene and phosgene dissolved in carbon bisulphide—about the only solvent not itself attacked by the metallic chloride. So I passed a stream of phosgene gas into a solution of anthracene (prepared by reduction of anthraquinone) in carbon bisulphide to which some powdered aluminium chloride had been added. When the solution was saturated with the gas,[2] I gradually heated it to boiling, without, however, a reaction taking place. No hydrochloric acid was given off and the whole of the anthracene was recovered from the solution.

CHICAGO, *September*, 1892.

THE DISSOCIATION OF SALTS INTO THEIR IONS BY WATER OF CRYSTALLISATION.

BY C. E. LINEBARGER.

It is well known that many salts which form crystalline compounds with water assume different colors according to whether they be in the anhydrous or hydrated state; also that the intensity of color varies according to the proportion of water present. Anhydrous copper sulphate, for instance, is white, while its several hydrates are blue. Aqueous solutions of copper sulphate are blue also. According to the electro-chemical theory of Arrhenius, this blue color of the solutions of copper sulphate is due to the presence of blue copper ions, for the SO_4 ions are colorless as well as the anhydrous molecule. Similarly all solutions of salts containing but one colored ion owe their color to that ion. In the case of salts, the anhydrous molecule as well as each of the ions of which are colored, the color of the solution is the resultant of the colors of the free ions and the undecomposed molecule. Now, if it be admitted that the color of a solution of a salt be due to the presence of colored ions, it must be admitted also that the color of the same salt crystallised with water of crystallisation is due to the presence of free ions, or, in other words, *the water of crystallisation has the power of dissociating crystallised salts into their ions.* Thus, in the example chosen, copper sulphate containing blue copper ions has a blue color if water of crystallisation or of solution be present; otherwise it is white. In the case of colorless salts composed of colorless ions, it follows from analogy that the above statement obtains also.

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[1] Graebe and Liebermann: Ber. d. chem. Ges. 2, 678.

[2] Phosgene is very soluble in carbon bisulphide.

Considerations of a somewhat different nature lead also to the conclusion that salts crystallising with water may decompose into their ions. The hard-and-fast line that was once supposed to separate the liquid from the solid state of aggregation does not in reality exist. Solids have the faculty of forming solid solutions,[1] which diffuse, exert an osmotic pressure, and, what is of vital importance for the question at issue, are in many cases conductors of electricity of the second class. The fact of electrolysis renders necessary the assumption of electrical dissociation. Vapors in many cases are true electrolytes; innumerable solutions have been found to be such, as well as many salts in the vicinity of their melting-points. So far as I know, no experiments have been carried out to test the electrical conductivity of salts containing water of crystallisation. The degree of dissociation of salts in solution is generally determined from the osmotic pressure or from the electrical conductivity. The methods in use may not be exactly suited to solids, but undoubtedly others will be found. Thus the experiments of Graetz[2] and Poincaré[3] show that at the melting-points of salts there is no abrupt change in the electrical dissociation or in the friction of the ions. Accordingly, it may be expected that at the melting-points of hydrated salts the electrical conductivity is the same in both liquid and solid state; knowledge

[1] J. H. Van't Hoff: Zeitschr. f. phys. Ch. **5**, 322.

[2] Wiedemann Ann. **40**, 18.

[3] Ann. de chim. et phys. (6) **21**, 289.

may thus be gotten of the degree of dissociation in the solid state. The investigation of the magnetic rotation and the refractive index will also contribute to our knowledge of the subject.

The most general conclusion drawn from the assumption of free ions in solution is that the properties of solution can be represented as binary sums of the properties of both ions. This conclusion must obtain also for salts crystallised with water. But as the conclusion in regard to solutions is strictly true only for infinite dilutions, we may expect to find many seeming exceptions in the case of crystallised salts where the concentration is very great. Still, from the data at hand, I think that it may be stated as a general law that *salts crystallising with water of crystallisation are more or less decomposed into their ions.*

CHICAGO, *September* 20, 1892.

THE IODOMERCURATES OF ORGANIC BASES.

BY ALBERT B. PRESCOTT.[1]

An iodide of mercury and an alkaloid is not merely a double halide of two unlike bases. In character it is not at all a mean between mercuric iodide on the one hand and an iodine compound of the alkaloid on the other. So far as it can be compared with any iodine compounds of alkaloids, it resembles the unions of free iodine more than the salts of hydriodic acid. But the element mercury joins its influence with that of the iodine to constitute an iodomercuric acid group of decided affinity for certain bases. These certain bases are those typified by pyridine and by the quinolines—tertiary bases carried in closed carbon chains.

An iodomercurate is evidently a strongly individualised compound, as, in a degree, a ferrocyanide differs widely from a mean between the simple cyanides of the two metals it contains. But the iodomercuric-acid group exhibits its character only with the nitrogenous aromatic bases. Iodomercurates are to be compared with chloroplatinates, and, in a degree, with chloraurates, hardly with alkaloidal halogen compounds of cadmium, or bismuth, though all these make some definite combinations with alkaloids.

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[1] Read at the Rochester Meeting of the American Association for the Advancement of Science, August, 1892.

As a free element iodine effects a class of combinations with alkaloids generally, such as bromine and chlorine fail to effect. Apparently iodine atoms, more readily than those of bromine or chlorine, link together in a polyvalent group binding two other groups to each other. Again two atoms or three atoms of iodine seem to take the place of a monovalent group, as hydroxyl or amidogen would. All these considerations require a systematic study of the iodine compounds of the alkaloids, and bear upon the structure of iodomercurates.

When there shall be a surer understanding of the linkings of nitrogen in such compounds as ferrocyanides, and of the linkings of pairs of halogen atoms, it will become profitable to compare the part of iodine in the metallo-iodides with that of cyanogen in metallo-cyanides.

The iodomercurates are chiefly known in literature as precipitated products of potassium-mercuric iodide. A solution of this double halide was announced as a reagent for alkaloids in 1827,[1] in 1829,[2] and in 1830.[3] In 1846, Planta-Reichenau[4] reported the use of the tenth-normal solution of the reagent, substantially as published by Mayer in 1861.[5] Just before this, Groves[6] reported a research "On some Compounds of Iodide and Bromide of Mercury with the Alkaloids." The volumetric factor of the decinormal solution has been the subject of work by Dragendorff,[7] and later, in this country, by Lyons and by Snow.[8]

Following mainly the purpose of Groves, with difference of method, the writer several years ago presented some determinations of the iodomercurates of several vegetable alkaloids.[9] These did not agree very well in all respects with the figures of Groves, though somewhat more consonant with rational formulæ. To leave least possible doubt of the results, full elementary analyses

[1] P. Boullay, 1827: Ann. der Phys. Pogg. **87**, 99; Ann. chim. phys. [2] **34**, 345.

[2] P. A. von Bonsdorff, 1829: Ann. der Phys. Pogg. **93**, 243.

[3] F. L. Winckler, 1830: "Buchner's Repertorium," **35**, 57.

[4] A. von Planta-Reichenau, 1846: "Das Verhalten der Alkaloide gegen Reagentien"—a dissertation at Heidelberg.

[5] F. F. Mayer, 1862: Am. J. Phar. **35**, 20; Chem. News **7**, 159; **8**, 177, 189.

[6] Thomas B. Groves, 1858: Chem. Soc. **11**, 97; Phar. J. Trans. **18**, 181.

[7] G. Dragendorff, 1874: "Werthbestimmung starkwirkender Droguen."

[8] A. B. Lyons, 1886: Am. J. Phar. **58**, 579. H. W. Snow, 1888: *Ibid.* **60**, 487.

[9] A. B. Prescott, 1880: This Journal **2**, 294.

of iodomercurates have been made by Mr. Lyman F. Kebler, and to report these is the chief object of this communication.

The precipitates were those of quinine, of pyridine, and of quinoline. The quinine was purified by Mr. Kebler, the sulphate being recrystallised from hot water three times, the crystals being washed each time with cold water. This salt was precipitated by sodium hydroxide, and the washed precipitate, brought to constant weight at 120° C., taken as material for the work.

Observers have so generally found, with different alkaloids, a variability in the volumetric value of Mayer's reagent, as well as a point of unstable equilibrium in its use, that it seemed desirable to determine the elementary composition of an iodomercurate precipitated in several different degrees of concentration. Therefore the purified quinine, as a sulphate, was precipitated from four solutions, in 25, 50, 75 and 100 parts of water respectively to one part absolute quinine. An excess of the reagent was avoided in the precipitation. The precipitates, washed with water, were dried to constant weight at 60° C., for the elementary analysis.

The method of elementary analysis, in view of the presence of mercury and iodine, was a matter of experimentation with Mr. Kebler, who settled upon a procedure as follows: In the combustion for carbon and hydrogen, two U-shaped "chloride of calcium tubes" loosely filled with glass wool, and otherwise empty, were interposed between the combustion tube and the chloride of calcium. The first U-tube receives mercuric iodide and mercury during the combustion, the second one does not. To recover all the water of combustion from the glass wool, the dry air current is continued through the apparatus, with the combustion tube hot, drawing the current with an aspirator, or with a water-pump provided with a large regulator, for three to five hours. Heat may not be applied to the tubes interposed for mercury, nor can the glass wool be substituted by asbestos.

The nitrogen was estimated in the direct method, without interference by the mercuric iodide. For the mercury, a weighed portion of the dry iodomercurate was dissolved in alcohol acidulated with sulphuric acid, and the solution treated with gaseous hydrogen sulphide for full precipitation. For the iodine, a weighed portion of the dry iodomercurate was dissolved in alcohol acidulated with nitric acid, and a saturated solution of silver nitrate added to complete precipitation. For both the precipitates so obtained, the mercury sulphide and the silver iodide, carbon tubes (such as are used in iron analysis) were prepared by placing a spiral of platinum in the bottom of each tube and filling over for about two centimeters in depth with finely-shredded asbestos suspended in water, then drying to a weight constant at 175° C. The two precipitates, for mercury and for iodine, were filled into the two tubes prepared, exhausted of liquid and washed with a filter-pump, and dried at 175° C., to a constant weight, when the weight of the prepared tubes was subtracted. This procedure was adopted by Mr. Kebler after trials of several other ways. Owing to the unusual features of the analysis, the results were obtained by Mr. Kebler in quadruplicate for each of the four quinine precipitates, and were as follows:

	I.		II.		III.		IV.	
C	20.92 21.10 21.12 20.92	21.01	20.86 20.69 20.43 20.91	20.87	20.82 20.66 20.78 20.71	20.74	20.96 20.67 20.72 20.70	20.72
H	2.27 2.19 2.26 2.24	2.24	2.49 2.25 2.21 2.33	2.32	2.41 2.73 2.29 2.37	2.45	2.21 2.73 2.43 2.34	2.42
N	2.53 2.41 2.35 2.51	2.45	2.33 2.31 2.34 2.30	2.32	2.51 2.32 2.26 2.42	2.38	2.89 2.57 2.36 2.24	2.51
Hg	23.13 23.16 23.21 23.12	23.20	23.15 23.12 23.56 22.96	23.28	24.03 22.27 23.29 22.81	23.10	23.20 23.36 23.66 23.49	23.42
I	47.59 47.51 47.68 47.70	47.62	47.22 47.60 47.59 47.39	47.45	47.41 47.56 47.25 47.35	47.39	47.21 47.36 47.40 47.53	47.42
O	3.56 3.63 3.35 3.51	3.51	3.95 4.03 3.87 4.11	3.99	2.82 4.46 3.74 4.34	3.84	3.53 3.33 3.43 3.51	3.41

It appears, therefore, that the composition of the precipitates is not varied by the dilution of the solution in which precipitation is effected. And all the results are in quite good agreement, giving redundant proof of the safety of the method. The errors are doubtless largest in the mercury, while the oxygen carries the sum of the errors of the other five elements.

For the formula $(C_{20}H_{24}N_2O_2)_2(HI)_3(HgI_2)_3.H_2O$, the centesimals stand as follows:

	Calculated.	Found, mean.
C	19.91	20.85
H	2.21	2.35
N	2.32	2.41
Hg	24.88	23.25
I	47.34	47.47
O	3.31	3.68

Mr. Kebler observed the solubilities of the iodomercurates of pyridine and quinoline. These bases are both precipitated from their salts by Mayer's reagent, the precipitation being permanent when the reagent is in excess. Both precipitates are slightly soluble in water. Iodomercurate of pyridine is soluble in alcohol, dilute or absolute, and in hot acetic acid of 40 per cent. It melts at 102°–103° C. Iodomercurate of quinoline is still more soluble in acetic acid.

A sample of pyridine was fractionated until a portion was secured with a constant boiling-point of 114.5° C. for several successive distillations. The hydrochloride of this body, acidulated with hydrochloric acid, was treated at 25° C. with the decinormal solution of potassium mercuric iodide, short of excess, the precipitate washed on a filter at 60° C., and dried at 60° C. to a constant weight. Elementary analysis by the procedure already describes gave figures, in triplicate, as follows, compared with the formula, $C_5H_5N(HgI_2)_2$:

	Calculated.	Found.			
		I.	II.	III.	Mean.
C	6.08	5.85	5.86	5.91	5.87
N	1.42	2.10	1.83	1.62	1.85
I	51.44	50.00	52.16	51.12	51.09
Hg	40.57	41.26	39.86	40.49	40.53
H	0.49	0.79	0.29	0.89	0.66

The hydrogen figures were obtained by difference.

A sample of synthetically-prepared quinoline was fractionated until a portion was obtained giving a constant boiling-point under constant low pressure, the last distillation being done in an atmosphere of dry hydrogen. The purified quinoline was treated for precipitation of iodomercurate, exactly as done for the pyridine compound. The precipitation was at 25° C., and the reagent not in excess. The centesimals were as follows, compared with the formula $C_9H_7NHgI_2$:

	Calculated.	Found.		
		I.	II.	Mean.
C	18.47	18.72	18.59	18.65
N	2.39	2.54	2.91	2.72
I	43.35	43.51	43.12	43.31
Hg	34.20	34.00	33.79	33.89
H	1.54	1.23	1.59	1.43

The reactions of pyridine with mercuric chloride, mercuric iodide, and metatungstic acid, upon pyridine, were obtained by Koenigs and Geigy in 1884.[1]

All discussion of the contrast between the pyridine and the quinoline iodomercurate is reserved for better data and further study. The question is of importance to inquiries of the linking of mercury, iodine and nitrogen, in alkaloids in general.

UNIVERSITY OF MICHIGAN, *August*, 1892.

TRIMETHYLXANTHINE AND SOME OF ITS DERIVATIVES.[2]

BY MOSES GOMBERG.

The constitutional formula of caffeine, as first proposed by Medicus[3] and afterwards modified by E. Fischer,[4] explains quite clearly all the decompositions of the alkaloid. Its probable correctness becomes so much more apparent when we remember that the formulæ for theobromine, theophyline[5] and xanthine have been derived from that of caffeine, and all the experimental evidence goes to corroborate the formulæ of the lower homologues of caffeine.

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[1] Ber. d. chem. Ges. **17**, 594.

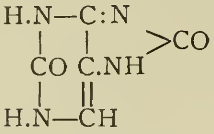
[2] Read by A. B. Prescott at the Rochester Meeting of the American Association for the Advancement of Science, August, 1892.

[3] Ann. Chem. (Liebig) **175**, 250.

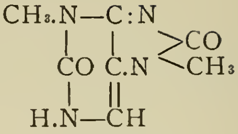
[4] *Ibid.* **215**, 253.

[5] Ztschr. physiol. Chem. **13**, 298.

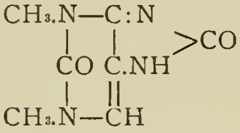
The formulæ for the four compounds are:



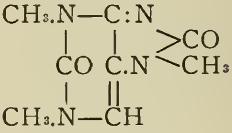
Xanthine.



Theobromine.



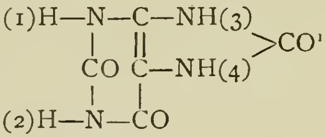
Theophyline.



Caffeine.

The presence of three imide groups in xanthine explains how it and its homologues, theobromine and theophyline, can act as acids, and how caffeine has no acid properties whatever.

But it is on comparing the properties and reactions of xanthine and its homologues on one hand, with those of uric acid and some of its homologues on the other, that the correct conception expressed by the respective formulæ becomes so much more clear. Like that of xanthine, the formula of uric acid,



explains how it and its homologues, mono-, di-, and even trimethyl-uric acid, can still act as acids, forming at least with some bases salt-like bodies. It is for this reason that we have a tetramethyl-uric acid,[2] while no corresponding derivative of xanthine has been prepared.

The important difference between these two classes of compounds is still more strikingly brought out by the difference in their behavior towards hydrochloric acid under pressure:

$$\left\{\begin{array}{l} C_5H_4N_4O_2 + 6H_2O = NH_3 + NH_3 + NH_3 + NH_2.CH_2.CO_2H + \\ \qquad H.CO_2H + 2CO_2{}^{3} \\ C_5H_4N_4O_3 + 5H_2O = NH_3 + NH_3 + NH_3 + NH_2.CH_2.CO_2H + \\ \qquad 3CO_2{}^{4} \end{array}\right.$$

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[1] Medicus: Ann. Chem. (Liebig) **175**, 230; E. Fischer: Ber. d. chem. Ges. **18**, 1776.

[2] E. Fischer: Ber. d. chem. Ges. **18**, 1784.

[3] E. Schmidt: Ann. Chem. (Liebig) **217**, 309.

[4] Strecker: *Ibid.* **146**, 142.

$$\left\{\begin{array}{l} C_5H_2(CH_3)_2N_4O_2 + 6H_2O = NH_2.CH_3 + NH_3 + NH_3 + \\ \quad NH.CH_3.CH_2.CO_2H + H.CO_2H + 2CO_2\text{[1]} \\ C_5H_2(CH_3)_2N_4O_3 + 5H_2O = NH_2.CH_3 + NH_3 + NH_3 + \\ \quad NH.CH_3.CH_2.CO_2H + 3CO_2\text{[2]} \end{array}\right.$$

$$\left\{\begin{array}{l} C_5H(CH_3)_3N_4O_2 + 6H_2O = NH_2.CH_3 + NH_2.CH_3 + NH_3 + \\ \quad NH.CH.CH_3.CO_2H + H.CO_2H + 2CO_2\text{[3]} \\ C_5H(CH_3)_3N_4O_3 + H_2O = \text{a crystalline compound, undeter-} \\ \quad \text{mined.[4]} \end{array}\right.$$

$$\left\{\begin{array}{l} \rule{5cm}{0.4pt} \qquad \rule{8cm}{0.4pt} \\ C_5(CH_3)_4N_4O_3 + 5H_2O = NH_2.CH_3 + NH_2.CH_3 + NH_2.CH_3 + \\ \quad NH.CH_3.CH_2.CO_2H + 3CO_2 \text{ (?)[5]} \end{array}\right.$$

It appeared to the writer of some scientific interest to make an attempt to prepare a tetramethylxanthine. Besides the physiological interest attached to it as a probable new alkaloid, the object was to determine, if possible, whether this new compound would break up under the influence of hydrochloric acid and pressure, with liberation of three substituted-ammonia molecules to one of free ammonia, as might be expected from the present structural formula of xanthine. Although the results are far from being complete, yet the writer begs leave to report them such as they are, however little light they throw upon the subject in question. The work done so far can be best treated of under separate sections:

I. Iodocaffeine.

II. Action of sodium upon a mixture of an alkyl-halogen and a halogen-caffeine.

III. Action of zinc ethyl upon halogen-caffeine.

IV. Action of potassium cyanide upon chlorocaffeine.

I. There are known two halogen-caffeines, $C_8H_9ClN_4O_2$ and $C_8H_9BrN_4O_2$. As both are very stable compounds, it was thought best to prepare a derivative more sensitive to the action of reagents; this, it was expected, would be found in iodocaffeine.

The ordinary method of introducing iodine into organic compounds,—namely, by treating the corresponding chloro- or bromo-compound with an iodide of a light metal,—proved in this case unsuccessful. First chlorocaffeine, then the bromo-compound, were heated with 2 to 3 times the theoretical quantity of sodium iodide, potassium iodide, and calcium iodide in alcoholic solutions, in flasks with inverted condensers. When filtered the liquids gave no indication of the presence of either chlorine or bromine.

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[1] For theobromine, *vid.* E. Schmidt: *loc. cit.*, p. 298.

[2] For β-dimethyluric acid [(3) and (4)], *vid.* E. Fischer: Ber. d. chem. Ges. **18**, 1780.

[3] E. Schmidt: *loc. cit.*, p. 278.

[4] E. Fischer: *loc. cit.*, p. 1783.

[5] *Ibid.*, p. 1784: "Decomposes like the other homologues, with liberation of methyl-amine, *but no ammonia.*"

The same trials were repeated by substituting sealed tubes for open flasks, at a temperature of 140°–150° C., but even then no change could be detected. An attempt was made to raise the temperature; at 195°–200° C., about two-thirds of the alcohol employed was converted into ether, by the hydriodic acid from the dissociation of the metallic iodide; all the halogen-caffeine was generally found to have been reduced to caffeine.

The experiments were repeated by using exactly theoretical quantities in absolute alcohol, but with similar results. Absolute ether was then substituted for the alcohol. The tube was heated for two weeks at 150° C., but no change could be noticed, except that some iodine was set free.

An attempt was next made to prepare iodocaffeine by direct substitution of iodine for hydrogen, in a manner analogous to that employed by E. Fischer in preparing chlorocaffeine. But the dark residue, obtained by heating a mixture of iodine and caffeine in chloroform, was at once decomposed on addition of water, with formation of caffeine. It was decided to isolate this addition-compound and examine it more closely; after several trials the following method was found to give satisfactory results:

Dry caffeine is dissolved in a suitable amount of anhydrous chloroform. The flask is connected with a Soxhlet's extraction-apparatus, in which a good supply of iodine is placed—about four times the quantity of caffeine employed. After several hours' action the chloroform is distilled, the dark residue is heated in an oil-bath to 140°–150° C., whereby the largest part of the excess of iodine is sublimed. The product is then powdered and placed in the extraction-apparatus. It is first exhausted for several hours with chloroform to remove the unchanged caffeine, then with carbon bisulphide till the latter shows only a very slight iodine coloration. The product is a dark granular powder, with no odor of iodine, almost insoluble in carbon bisulphide, ether, chloroform; quite permanent on exposure to air, but on addition of water or alcohol it immediately decomposes with liberation of caffeine and iodine.

An elementary analysis gave the following results:

I. 0 9614 gram substance gave 0.4237 gram CO_2 and 0.1318 gram H_2O.

II. 0.3127 gram substance gave 0.1367 gram CO_2 and 0.0404 gram H_2O.

III. 0.4283 gram substance gave 0.1772 gram CO_2 and 0.0603 gram H_2O.

IV. 0.2106 gram substance gave 13.2 cc. N at 22° C. and 741.7 mm.

V. 0.3762 gram substance gave 23.2 cc. N at 22° C. and 741.7 mm.

VI. 0.4303 gram substance gave 27.3 cc. N at 25.3° C. and 729.9 mm.

VII. 0.5461 gram substance gave 0.4110 gram I.

VIII. 0.4607 gram substance gave 0.3482 gram I.

IX. 0.1628 gram substance gave 0.1238 gram I.

Combustions I and II were made by mixing the substance with copper oxide; combustion III, by using lead chromate.

Determinations VII and VIII were made by suspending the substance in water, treating with sulphur dioxide, and precipitating with silver nitrate. Determination IX was made by igniting the substance with lime.

	Calculated for $C_8H_{10}N_4O_2.I_5$.				Found.			Mean.
C	11.61	(I)	12.02	(II)	11.63	(III)	11.29	11.65
H	1.21		1.52		1.43		1.56	1.50
N	6.77	(IV)	6.93	(V)	6.82	(VI)	7.10	6.95
I	76.54	(VII)	75.26	(VIII)	75.57	(IX)	76.03	75.62

When suspended in water and treated with standard sodium thiosulphate the compound gave, as a mean of four estimations, 60.05 per cent. of iodine, showing that only four atoms of iodine are addition-atoms, the fifth having an entirely different function in the molecule.

In 1865 Tilden[1] obtained an "iodocaffeine" by dissolving caffeine in a weak alcoholic solution of hydriodic acid. The compound, according to Tilden, is very unstable, does not stand the heat of a water-bath, and is to be dried *in vacuo;* its formula is $(C_8H_{10}N_4O_2.HI).I_2 + H_2O$. But the compound prepared by the writer was dried at 95° C., cannot possibly have any water of cystallisation, and can hardly contain hydriodic acid as such.

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[1] J. Chem. Soc. (new series) **8**, 99.

Heated for three hours in an air-bath at 70° C., 1.3218 grams of the substance lost only 0.0026 gram = 0.19 per cent.; then on being again heated for three hours at 100°–110° C. it began to fuse slightly and lost 0.0129 gram = 0.97 per cent. Awaiting further experimental proof, the writer is inclined to think that the compound might be a tetraiodide of iodocaffeine, the latter being very unstable.

II. The action of sodium upon a mixture of an alkyl-halogen and a halogen-caffeine did not give satisfactory results. A great drawback to the successful application of this reaction was found in the fact that the halogen-caffeines are hardly at all soluble in ether, benzene, toluene, rhigolene, etc.

III. The action of compounds of zinc with aliphatic radicles upon halogen compounds is generally accompanied with great evolution of heat, and a diluent, such as ether, is usually employed. But neither chloro- nor bromocaffeine was acted upon when treated in this way. After distilling the ether the temperature had to be raised above 100° C. to distil the last portion of zinc ethyl. The solid residue was washed with hot water, but the latter showed only a minute trace of chlorine or bromine.

Pure zinc ethyl was next employed. This reagent was freshly prepared by Gladstone and Tribe's[1] method, and distilled directly from the couple upon a quantity of chlorocaffeine, the receiver being immersed in ice-water. The mixture was then gradually heated to 160° C. and kept at this temperature for 3 hours. At about 120° the halogen-compound all dissolved in the zinc ethyl, but on cooling separated again as a heavy white crust. The excess of zinc ethyl was distilled directly upon some bromocaffeine. The residue was exposed to air for some time, then washed with hot water; but the latter gave only a slight test for chlorine. The residue was proved to be unchanged chlorocaffeine, which is almost insoluble in water.

The bromocaffeine was now subjected to the same treatment as described above. It also dissolved at about 120° C., but to a dark solution, and on cooling separated as a dark-yellow crust. After removing the excess of zinc ethyl by distillation, the residue was washed with hot water, and the latter was found to contain a large amount of bromine.[2] The attempt to obtain the compound pure enough for analysis failed. The experiment was repeated on a larger scale, but the compound has not yet been obtained of sufficient purity.

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[1] J. Chem. Soc. 1879, **1**, 571.

[2] Bromocaffeine, like the chloro-compound, is almost insoluble in water, and does not precipitate silver nitrate.

IV. By the action of potassium cyanide upon a halogen-caffeine it was expected to prepare cyanocaffeine; this by further special treatment should give methyl-caffeine. 15 grams potassium cyanide were dissolved in about 600 cc. of 80 per cent. alcohol, the hot solution was filtered, and to it were added 30 grams of chlorocaffeine, which easily dissolved on heating. The hot solution was once more filtered and then boiled with an inverted condenser for three hours. By that time a heavy, yellowish sediment came down. This was separated by filtration, washed with hot alcohol, dilute hydrochloric acid, and finally hot water; dried at 110° C. The yield was 21 grams. Subjected to elementary analysis it gave the following results:

	Calculated for $C_8H_9(CN)N_4O_2$.	Found. I.	 II.	 III.
C	49.31	46.27	...	...
H	4.12	5.13	...	...
N	31.96	...	29.70	30.10

The experiment repeated with 25 grams chlorocaffeine and 12 grams potassium cyanide yielded 18 grams, with similar results upon analysis.

Fearing that the material prepared as described might contain some impurities, several portions of it were dissolved separately in large quantities of glacial acetic acid, in which solvent the compound is but slightly soluble—and solution filtered while hot. On cooling, white, somewhat crystalline deposits separated. They were washed with warm glacial acetic acid, then with hot water, and finally dried at 125° C. The different precipitates were analysed independently, and furnished the following results:

I. 0.2735 gram gave 0.4587 gram CO_2+0.1239 gram H_2O.
II. 0.3878 gram gave 0.6563 gram CO_2+0.1764 gram H_2O.
III. 0.2695 gram gave 0.4492 gram CO_2+0.1284 gram H_2O.
IV. 0.1453 gram gave 38.3 cc. N at 17° C. and 736 mm.
V. 0.2013 gram gave 53 cc. N at 20° C. and 736 mm.
VI. 0.2208 gram gave 60.5 cc. N at 21.5° C. and 736.5 mm.
VII. 0.2260 gram gave 61 cc. N at 26° C. and 739 mm.
VIII. 0.1574 gram gave 40.9 cc. N at 18° C. and 745 mm.
IX. 0.0856 gram gave 22.3 cc. N at 22° C. and 744.2 mm.

Combustions IV, V and VI were made in a platinum boat. In combustion VII a copper boat was used and the substance was mixed with copper oxide in the boat. In VIII and IX a closed tube was employed and the substance was mixed with the copper oxide in the tube.

Calculated in percentage the results are:

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
C	45.73	45.92	45.50	...	...	...	...	...	...
H	5.03	5.05	5.28	...	...	...	...	...	...
N	...	...	...	29.60	29.18	30.11	30.09	29.41	28.89

It is clear from an inspection of the results that the compound is not *cyanocaffeine.* According to E. Fischer,[1] prolonged boiling of bromocaffeine with a dilute alcoholic solution of potassium cyanide results in the production of a small quantity of *amidocaffeine.* It is reasonable to suppose that chlorocaffeine would act towards potassium cyanide as the bromo-compound does. But the writer is inclined to think that Fisher's compound is not *amidocaffeine,* for chlorocaffeine at least does not give that, as is seen on comparing the results with the theoretical figures:

	Calculated for $C_8H_9(NH_2)N_4O_2$.	Found (mean of the foregoing 9 determinations).
C	45.90	45.70
H	5.30	5.12
N	33.50	29.56

It would also be difficult to find an explanation for the formation of an amido-compound in this case. Potassium cyanate, nearly always present, could account for the production of only a small amount of amidocaffeine, while the yield obtained was in both cases about 85 per cent. of the theoretical value. Of course, if we assume that *isocyanocaffeine* is the first product of the reaction, then we can easily see how it can give rise to amidocaffeine. But there is no reason to make such an assumption.

On the other hand, however, if we suppose the action to be normal we can find an explanation. We may assume that the product is a half-saponified cyanocaffeine, resulting probably thus:

$$C_8H_9(Cl)N_4O_2 + KCN = C_8H_9(CN)N_4O_2 + KCl$$
$$C_8H_9(CN)N_4O_2 + H_2O = C_8H_9(CO.NH_2)N_4O_2.$$

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[1] Ann. Chem. (Liebig) **215**, 266.

Further saponification would give:

$$C_8H_9(CO.NH_2)N_4O_2 + H_2O = C_8H_9(CO.OH)N_4O_2 + NH_3.$$

The comparison of the theoretical figures with the results obtained would especially suggest that reaction.

	Calculated for $C_8H_9(CO.NH_2)N_4O_2$.	Found.
C	45.56	45.70
H	4.56	5.12
N	29.54	29.56

The production of an acid-amide from a cyano-compound without the help of either acid or alkali is somewhat rare but not altogether unusual; so when benzyl chloride, $C_6H_5.CH_2Cl$, is heated with potassium cyanide, besides the normal product benzyl cyanide, $C_6H_5.CH_2CN$, phenylacetamide, $C_6H_5CH_2.CO.NH_2$, is also produced.

The supposition of this being the case here might be justified (1) by the results of the elementary analysis of the compound; (2) by the probability of the reaction; and (3) by the behavior of the compound. Although all attempts to prepare carboxy-caffeine have so far failed, yet some of the results are suggestive. When the compound described is treated with potash in alcohol, or with strong hydrochloric acid, in sealed tubes at 130° C., or with H_2SO_4(1 : 1) at 100° C., it breaks up into *caffeine and carbon dioxide*, pointing to the intermediate formation of carboxy-caffeine, which, however, under the conditions employed is not stable.

In conclusion I must express my thanks to Mr. A. W. Augir, who kindly helped me in determining the elementary composition of the compounds used and prepared.

UNIVERSITY OF MICHIGAN, *August*, 1892.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

No. XVIII.

Communicated by F. P. DUNNINGTON.

151.—ANALYSIS OF CUPROPLUMBITE FROM BUTTE CITY, MONTANA.

BY J. T. DE BELL.

This mineral was received with some other ores from the Canton Copper Co., of Baltimore. It is amorphous, of bluish-gray black color, lustre sub-metallic, fracture uneven, fuses with spurting, sp. grav. = 5.39, hardness = 2.5, and upon analysis presents the following composition:

		Atomic Ratio.
Copper	61.32	10.51
Lead	18.97	1.00
Sulphur	17.77	6.01
Silica (quartz)	1.58	...
	99.64	

Which gives approximately the formula, $5Cu_2S.PbS$.

In Dana's Mineralogy[1] mention is made of three varieties of cuproplumbite, viz:

$Cu_2S.2PbS$
$2Cu_2S.PbS$
$3Cu_2S.PbS$

The specimen before us adds, therefore, another member to this series.

The question is also raised[2] as to whether these compound sulphides are to be classified with galena or with chalcosite.

If we consider galena as having sp. grav. = 7.5, and imagine in each 6 molecules that 5 atoms of lead (5Pb) are replaced by 10 atoms of copper ($5Cu_2$) without altering the aggregate bulk of the molecules, this will give the sp. grav. = 5.45.

If, on the other hand, we take chalcosite (sp. grav. = 5.7) and similarly in 6 molecules replace Cu_2 by Pb, then its calculated sp. grav. = 6.16.

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[1] 6th edition, page 51.

[2] Loc. cit.

Now the mineral under discussion has the sp. grav. = 5.39, and when this is corrected for the quartz present it gives 5.43, which nearly coincides with the above calculated sp. grav. 5.45 obtained when it is regarded as built in the form of galena. From this it appears that the mineral is to be classed with isometric galena.

152.—ANALYSIS OF ELECTRIC CALAMINE FROM WYTHE COUNTY, VIRGINIA.

By Archibald Jones.

This mineral is found on New River, in the mines belonging to and now worked by the Bertha Zinc Company, of Pulaski, Va.

Some years ago, an analysis made in this laboratory was published,[1] showing that the snow-white opaque sheets of ore from this mine consist of electric calamine containing a slight excess of zinc oxide and water.

Encrusting the material above-mentioned there is occasionally found a layer of bright, transparent, colorless crystals 1 to 2 mm. in thickness. Some of this layer was carefully removed and afforded the following results: specific gravity = 3.40; hardness = 4.9; and composition:

		Calculated for $Zn_2SiO_4 + H_2O$.
Silica	25.33	25.0
Zinc oxide	67.15	67.5
Water	7.47	7.5
	99.95	100.0

From which it appears that these crystals present a peculiarly pure specimen of electric calamine.

153.—ANALYSES OF TSCHERNOZEM OR BLACK SOIL.

By F. P. Dunnington and T. C. Whitlock.

With several specimens of typical soils from British America, kindly furnished me by Dr. Geo. M. Dawson, F. R. S., Ottawa, Can., there was one from the prairie land of Red River, taken at Rossers, about 15 miles west of Winnipeg, Manitoba, which presented so marked similarity in appearance to the black soil of

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[1] Chemical News, 731.

Russia that I thought it would prove interesting to make such comparison of the general nature of these soils as is expressed by a chemical analysis of the two.

Among some specimens of Tschernozem or Black Earth of Russia sent to me by Prof. Nicolas Menschutkin, of St. Petersburg, darkest in color, was one from the land of M. Naroushkin, District Balashoff, Government Saratoff. These two specimens, which are so similar in appearance that they are not to be distinguished by the eye, have been analysed by Mr. Whitlock with the following results:

	Manitoba.	Russia.
Sand,	59.82	53.71
Silica, amorphous,	5.45	12.80
Ferric oxide,	4.00	4.13
Alumina,	7.14	6.04
Titanic oxide,	.64	.63
Lime,	.61	.75
Magnesia,	.61	.21
Sulphuric oxide,	.03	.06
Carbonic oxide,	.37	.02
Phosphoric oxide,	.13	.16
Potash (with trace of soda)	1.91	1.97
Organic matter,	12.49	14.91
Containing humus,[1]	(.45)	(.44)
" total nitrogen,	(.44)	(.31)
Water,	6.86	5.04
	99.76	100.43

This analysis of the Russian black earth fairly agrees with published analyses of other specimens of it.

With the exception of the amounts of carbonic acid and of the proportion of the silica which is amorphous, the composition of these two specimens is almost identical.

The peculiarly large amounts of organic matter and nitrogen, as well as of the principal constituents of the ash of plants, lime, potash and phosphoric acid, are all to be noted and accord with the well-known exceeding fertility of each of these soils.

The soil from Manitoba is described by Dr. Dawson[2] as "spread with great uniformity over the Red River valley, a wide prairie on the first or lowest prairie level of the Northwestern country. It has a depth of say one to four feet, and consists of the superficially modified parts of the sediments of a later glacial or post-glacial lake, which at greater depths are found in the form of well-bedded silts. . . . Within the province of Manitoba it covers an area of not less than several thousand square miles. . . . The surface is a dark mould, composed of the same material as the subsoil, but mingled with much vegetable matter. . . . The uniform fertility of this soil cannot be exaggerated."

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[1] Soluble in ammonia.

[2] In a private letter and in report on the Geology of 49th Parallel, 1875.

The Tschernozem or Black Earth of Russia has long been famous by reason of the heavy crops which it has, in many localities, annually produced for almost a century. Prof. Krassnof, in a paper[1] upon this subject, describes it as distributed over the steppes of the southeastern portion of European Russia. He concludes that this black color is due to an accumulation of vegetable matter from the herbaceous plants of the poorly drained steppes of the post-glacial deposits which overlie the loessoid clays, so difficultly permeable to water. At the close of this paper he draws attention to the close correspondence which exists between the climate of Russsia and that of the prairie land of Minnesota (much of which lies in the Red River valley) and suggests the probable similarity of the soils of these regions.

The above analyses make it to appear that the Tschernozem and the soil of the Red River prairies are similar in chemical composition; they occur in the same latitude, with the same general relief and climate, and from the above quoted authorities are judged to have a similar geological history; may they not therefore be properly considered as of the one variety of soil, "Black Earth"?

154.—ANALYSIS OF WASHING POWDERS.

BY W. J. KINNEY, W. H. WENGER AND F. P. D.

The various washing powders used as substitutes for soap present a conspicuous example of substances in general use which are usually employed with little understanding of their nature or composition.

The four samples selected are of such powders for washing clothes, etc., largely sold in Virginia, and a knowledge of their composition will prove of interest to many. Analysis afforded the following results:

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[1] Proc. Geolog. Soc. America, Washington Meeting, 1891, page 68.

	A.	B.	C.	D.
Sodium carbonate	45.2	26.9	49.2	46.6
Fatty acids	26.4	44.0	25.6	25.7
Combined soda	3.1	3.4	3.5	2.6
Fine sand	...	16.3	...	...
Water	23.7	8.8	19.1	24.9
	98.4	99.4	97.4	99.8

A portion of this water is necessarily in the soap, and the remainder is with the sodium carbonate, which has in each case been partially dried. The soaps used do not contain rosin. Not a trace of borax was present.

We may therefore describe these substances as generally composed of a mixture of soap and dried washing soda, both powdered.

While a small amount of such powders may properly be employed, in conjunction with soap, to remove the "hardness" of the water when washing textile fabrics, yet the substitution of any such powders for soap must result in a gradual corrosion of cotton, linen or woolen goods.

Borax might be employed in place of soda in the above preparations with great advantage (to all except the manufacturer), since it has no corrosive action upon such fabrics, and, while it removes all hardness from the water, is also an excellent detergent.

155.—SOLUBILITY OF CREAM OF TARTAR IN DILUTED ALCOHOL.

By W. H. Wenger.

The solubility of cream of tartar in water, wine and other liquids at varying temperatures has been carefully studied by M. Chancel; but no figures are given for other dilute alcohol than that of 10.5 per cent.

With a view to use in some analytical processes the following determinations were made.

Measured amounts of a saturated aqueous solution of cream of tartar were mixed with the calculated amount of 92 per cent. alcohol, to give residual liquids of the desired strength of alcohol. These were repeatedly shaken and allowed to stand for some days at a temperature of approximately 25° C., and then measured amounts of the liquids were filtered off and titrated with decinormal solution of sodium hydrate, using phenolphthalein as the indicator. The following results were obtained:

Grams of cream of tartar dissolved in 1000 cc. of—

Alcohol of 90 per cent.	.15
80 "	.19
70 "	.30
60 "	.41
50 "	.79
40 "	1.32
30 "	1.96
20 "	3.01
10 "	4.51
Water	5.75

It is proposed to enlarge this table by obtaining these estimates of solubility for other temperatures.

156.—ANALYSES OF KALE AND TURNIP SALAD AND OKRA.

BY J. D. TINSLEY.

Both of the specimens of salad were gathered and analysed in April. The kale was weighed promptly after cutting. The turnip salad was cut some hours before being weighed, when it had wilted somewhat, hence the larger proportion of solid matter which it contains in the "fresh" leaves (this was not noted until the analysis was nearly completed). The specimen of okra pods was cut in August, weighed immediately, sliced, dried and analysed the next April.

The analyses were conducted by the scheme presented by the American Association of Agricultural Chemists and afforded the following:

100 parts of the "fresh" plant.	Kale salad.	Turnip salad.	Okra pods.
Water by air-drying	88.34	77.78	83.07
Water at 212°	1.32	2.27	1.64
Solid matter	10.34	19.95	15.29
Solid matter containing:			
Pure ash	1.22	2.62	.91
Ether extract	.65	1.59	.29
Crude fibre	1.15	1.57	1.44
Crude starch, gum, etc.	3.43	8.07	10.12
Crude protein	3.89	6.10	2.53
Nitrogen total,	.62	1.12	.41
Nitrogen albumenoid,	.25	.68	.28

Composition of, Dried at 100°.	Kale salad.	Turnip salad.	Okra pods.
Ash, pure	11.83	13.15	6.65
Ether extract	6.35	8.01	2.02
Crude fibre	11.16	7.93	9.39
Crude protein	37.75	35.12	18.37
Starch, etc., by diff.	32.91	35.79	63.57

No doubt the dietetic value of these vegetables is not to be reckoned solely by the nutrients which they contain, yet in view of their very general use as food, their composition is a matter of interest. The large amount of protein in the salads, as shown in the latter table, is of special note, in that it is even greater than in dried beans or peas, which are ordinarily instanced as most highly nitrogenous of the vegetable foods of man.

157.—ANALYSIS OF STATUARY MARBLE FROM RUTLAND, VERMONT.

By Jno. T. De Bell.

This marble is now extensively quarried for building purposes, and being quite uniform as well as moderately fine in texture, it is also employed for statuary other than the finest work. It is occasionally marred by pale greenish seams, showing minute foreign crystals.

A sample free of visible seams was furnished by Edw'd V. Valentine, Esq., of Richmond, Va., and this upon analysis showed the following impurities in 100 parts:

SiO_2	0.167
Fe_2O_3 and Al_2O_3	0.062
Na_2O	0.065
K_2O	0.004
MgO	0.079

corresponding to the composition:

Calcium carbonate	99.536
Magnesium carbonate	0.174
Other impurities	0.290

An examination of Carrara marble shows it to contain:

Na_2O(K_2O trace) . . . . 0.046 per cent.

hence lime made from the latter presents but little superiority to that from Vermont marble, when employed in analysis for the separation of magnesia from alkalies.

158.—ANALYSES OF GLAUCONITE FROM HANOVER COUNTY, VIRGINIA.

By M. B. Corse and Chas. Baskerville.

The extensive beds of greensand marl which occur in portions of Hanover, Chesterfield, Caroline, Prince William, Spottsylvania and Stafford counties vary greatly in depth and in the amount of potash contained. Among the richest of these deposits are beds from 3 to 6 feet in depth upon the farm of Maj. Winston, near Hanover Court House, which have a total potash content of from 1 to 2 per cent.

By washing the marl the clean glauconite was separated, and possessed the following properties and composition. Under the microscope it appears as rounded green grains interspersed with seams of quartz and with some spots of a much deeper green color than the main portion. It is almost insoluble in strong acids, but after gentle ignition, by which it loses water and becomes brown, it may be completely gelatinised by hydrochloric acid. Ignited in a closed glass tube, it becomes black. Of A, sp. grav. = 2.83; fusibility = 4.5.

Samples A and B were similarly obtained from different beds in the same vicinity; analysis of these affords:

	A.	B.
SiO_2 combined	47.45	43.34
Quartz	2.76	8.22
Al_2O_3	7.33	6.62
Fe_2O_3	12.03	15.16
FeO	9.43	8.33
MgO	2.90	.95
CaO	.57	.62
K_2O	5.75	4.15
Na_2O	.42	1.84
H_2O	9.85	10.32
	98.49	99.55

This considerable variation in the composition of the glauconite from contiguous beds but confirms the opinion that the mineral is a mixture. Any mechanical separation of the dark and pale green portions of these specimens would be impossible.

159.—ANALYSIS OF PARANTHITE, FROM CLAY COUNTY, NORTH CAROLINA.

By W. N. Berkeley.

This mineral was found by Mr. C. G. Memminger when superintendent of the mines of the Hiawassee Corundum Company, situated five miles southeast of Hayesville, N. C., who describes its occurrence as follows:

About ten pounds of the mineral, in rounded masses, of a few ounces weight each, was found at No. 2 mine, in a pocket near the centre of a six-foot vein, consisting of decomposed albite, corundophilite, chlorite, vermiculite and other chloritic minerals, lying between chrysolite and hornblende gneiss. Corundum is scattered through the vein-matter in grains and crystals varying in size from minute particles up to pieces weighing one-half a pound. During a year's work only this one pocket of the mineral was observed.

It consists of rounded crystalline lumps of a bluish-grey color. Sp. grav. = 2.75; hardness = 5.5; and upon analysis afforded the following:

		Oxygen Ratio.
SiO_2	47.54	4.7
Al_2O_3	34.03	3.
CaO	17.23	1.
Na_2O	1.82	
H_2O	1.02	

Since no chlorine is present, this mineral scarcely admits of being considered as a mixture of meionite and marialite, as it has been suggested by Tschermak[1] to express the composition of all such minerals; but it is rather to be designated as paranthite, in that its analysis closely resembles that of the mineral from Pargas,[2] to which Wolff assigned this name.

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[1] Dana's Mineralogy, 6th ed., p. 466.

[2] Dana's Mineralogy, 5th ed., p. 319.

PROTEIDS OF THE FLAX-SEED.

By Thomas B. Osborne.

The extensive use, as a cattle-food, of flax-seed partly freed from oil by expression or extraction, under the name of linseed-meal, renders desirable as complete a knowledge as possible of its chemical composition. As the chief value of this feed is due to the large amount of albuminoids contained in it, a careful study of these bodies is important from a practical as well as from a scientific standpoint.

Although extended examination of the literature of the vegetable proteids has been made, the writer has nowhere found any investigation relating to the proteids contained in this seed. A study of these proteids was accordingly undertaken, the results of which are given in this paper.

I.—Preliminary Experiments.

Ground flax-seed freed from oil by extraction with benzine or ether yields to both water and solutions of sodium chloride a large proportion of its proteid matter. After complete exhaustion with water, 10-per cent. sodium chloride brine extracts a further portion of proteid. Neither water nor salt solution removes all the proteids, for there always remains in the extracted residue more or less proteid soluble in dilute potash-water, as well as some nitrogenous substance, probably proteid, which the latter reagent fails to remove. Of the substance soluble in water or sodium chloride solution, a very large part is a globulin which has been separated in a crystalline form and prepared in a state of purity.

1. *Reactions of the Aqueous Extract.*

Very dilute acetic acid added to the aqueous extract of the meal gave a precipitate soluble in a slight excess of acid, but reprecipitated upon adding sodium chloride. Boiling produced a coagulum and great turbidity. Filtered from the coagulum, the hot solution gave a heavy precipitate with acetic acid, soluble in an excess, but reprecipitated upon adding sodium chloride. Saturation with ammonium sulphate completely precipitated the proteids. Saturation with sodium chloride gave no precipitate. Dilution with water was without effect. Prolonged dialysis produced but a trifling separation of the proteid. On standing for some days a considerable deposit, soluble in sodium chloride solution, separated. Heated slowly in a double water-bath, the extract became turbid at 50° C., a few flocks separating at 60°. Filtered after heating to 65° and again heated, the solution became turbid a second time at 70°, and flocks in minute amount formed at 78°. Filtered at 80°, a third turbidity developed at 82°, some flocks forming at 88°. Filtered at 90° and boiled, a coagulum was produced.

2. *Reactions of the Sodium Chloride Extract.*

An extract of the meal made with 10-per cent. sodium chloride solution gave the following results:

Dilute acetic acid produced a precipitate not noticeably soluble in an excess of dilute acid, but completely soluble in an excess of strong acid when hot and nearly so when cold. Boiling gave a very little coagulum, the filtrate from which, with dilute acetic acid, yielded a heavy precipitate. Saturation with ammonium sulphate completely precipitated the proteids. Saturation with sodium chloride caused a slight precipitate. Dilution with water gave a small precipitate after standing which, in some cases, was crystalline. Heated slowly, the clear solution became turbid at 45°, flocks appearing at 58°. Filtered at 63°, the solution became turbid again at 65°, and a few flocks developed at 76°. Heated to 80° and filtered, a turbidity appeared at 85° and flocks at 88°. Filtered at 90°, a coagulum formed on boiling, the filtrate from which gave a precipitate with dilute acetic acid which was soluble in a large excess of strong acid.

3. *Reactions of the Sodium Chloride Solution of the Separated Globulin.*

A solution prepared by dissolving the globulin in 10-per cent. sodium chloride brine had the following properties, which are here stated so that the reactions of the extract may be better understood.

Dilute acetic acid gave a heavy precipitate mostly soluble in a large excess of strong acid in the cold, and completely soluble on heating. Boiling yielded a little coagulum, the filtrate from which gave a heavy precipitate on adding acid. Saturation with ammonium sulphate caused a complete precipitation of the proteid. Saturation with sodium chloride produced a small precipitate. Dilution with water caused a small precipitate. Heated slowly the solution became turbid at 57°, flocks forming at 67°. Filtered at 72°, it became turbid again at 75° and developed flocks at 80°. Filtered at 85°, turbidity began at 85°, flocks forming at 88°. Filtered and boiled, a coagulum formed, the filtrate from which gave a large precipitate with acetic acid, soluble in a considerable excess of hot acid.

The reactions of these three solutions differed in the following respects:

With very dilute acetic acid the aqueous extract gave a precipitate soluble in a slight excess of acid, whereas the other solutions gave a precipitate soluble only in a large excess of strong acid. The cause of this difference lies in the fact that vegetable globulins are soluble in a very slight excess of acid in the absence of salts, but are insoluble in their presence, the insolubility increasing with the amount of salts.

Saturation with sodium chloride gave no precipitate in the aqueous extract, while in the other solutions it produced a small precipitate. This difference might be explained by the supposition that the salt solution extracted globulins insoluble in the salt solutions derived from the mineral constituents of the seed, were it not for certain observations on the coagulation-points soon to be described.

The heat-coagulation temperatures of these solutions are given in the following table:

HEAT-COAGULATION-POINTS OF THE

	Aqueous extract.	10-per cent. sodium-chloride extract.	10-per cent. sodium-chloride solution of the globulin.
1st. Turbidity,	50°	45°	57°
Flocks,	60°*	58°*	67°*
Filtered at	63°	63°	72°
2d. Turbidity,	70°	65°	75°
Flocks,	78°†	76°†	80°†
Filtered at	80°	85°	85°
3d. Turbidity,	82°	85°	85°
Flocks,	88°	88°	88°
Filtered at	90°	90°	90°
Boiling gave a	coagulum.	coagulum.	coagulum.

* Greatest in amount.

† Least in amount.

The two extracts agree well with each other, but the first and second coagulation-points of the solution of the globulin are 10° higher. This difference is probably due to the fact that the extract had a decided acid reaction, while the solution of the globulin was perfectly neutral. These heat-coagulation-points leave little doubt that they belong to the same bodies in all three solutions.

These coagulation-points indicate that besides the globulin separated from the extract in the crystalline form there are other globulins present in small amounts, which coagulate below boiling. This is shown by the fact that when a strong solution of the crystalline globulin in 10-per cent. brine is saturated with sodium chloride and, after filtering and diluting so that the solution again contains 10-per cent. sodium chloride, it is tested by carefully heating, the solution remains perfectly clear until heated to 73°, when it becomes turbid and separates a minute amount of flocculent matter at 82°. Heated to boiling, after filtering off this very minute coagulum, only an insignificant amount of the substance coagulates, but on adding acid a very heavy precipitate is thrown down. Furthermore, when the slight precipitate formed by saturating the 10-per cent. sodium chloride solution of the globulin with salt is washed with a saturated brine (so as to remove the dissolved globulin) and then taken up in a little water (so that the resulting solution of sodium chloride may contain 10 per cent. of this salt), the coagulable globulins are thus separated from the crystalline globulin. Coagulation-tests of a solution thus prepared gave the following results, which are given together with those obtained with a 10-per cent. sodium chloride solution of the original mixed globulins:

COAGULATION-POINTS OF THE SALT SOLUTION OF THE

	Precipitate produced by saturation with sodium chloride.	Original mixed globulin.
Turbidity,	59°*	57°*
Flocks,	68°	67°
Filtered at	72°	72°
Turbidity,	78°†	75°†
Flocks,	83°	80°
Filtered at	86°	85°
Turbidity,	. .	85°
Flocks,	89°	88°
	Increased very little on boiling. Some precipitate with acid.	Increased on heating to boiling, a considerable coagulum being formed. A very large precipitate with acid.

* Most in amount.

† Least in amount.

It is thus seen that the globulins coagulating below 90° are almost entirely removed by saturation with sodium chloride and that their amount is extremely small; accordingly, no further attempt was made to separate them, there being no probability of obtaining preparations fit for analysis.

A coagulation-test of the filtered and salt-saturated solution of the globulin showed a turbidity of 73° and minute flocks at 82°, indicating that the globulin coagulating at this temperature is only partly removed from the solution by saturation with sodium chloride.

These coagulable globulins were found to be much more soluble than the crystallisable globulin, in dilute solutions of sodium chloride; for on extracting the separated globulins with ½-per cent. sodium chloride brine, nearly the whole of these coagulable proteids was removed.

II.—EXTRACTION OF THE GLOBULIN.

1. *Extraction with pure water at* 20° *C.*—The ground flax-seed was freed from oil by extracting with benzine, and from the greater part of the outer coating of the seed by sifting through a fine sieve. The meal thus prepared, when air-dry, contained 8.40 per cent. of nitrogen—equivalent to 52.50 per cent. of proteids, assuming these to contain 16 per cent. of nitrogen. 100 grams of this meal were extracted with distilled water. The filtered extract had a strong yellow color, distinct acid reaction, and was very slightly turbid. The residue was then twice again extracted with distilled water, and the three extracts, after filtering, were united and saturated with pure ammonium sulphate. These operations were completed within 24 hours. The very abundant precipitate thus produced was collected on a filter and, after the solution had all run off, was removed from the paper and dissolved in about 800 cc. of water. This solution was then filtered perfectly clear and placed in a dialyser. After 24 hours a considerable precipitate had formed, which was seen under the microscope to consist entirely of perfectly formed octahedral crystals. After dialysing five days this solution was free from chlorides, the precipitate was then filtered off and the clear filtrate returned to the dialyser. Under the microscope the precipitate was found to be almost entirely composed of crystals, but a few spheroids were found among them. The deposit adhering to the paper contained some

very large particles which appeared crystalline to the naked eye. The precipitate was washed with water; dilute alcohol gradually increased in strength to absolute alcohol; then with ether, and dried over sulphuric acid. This preparation (1) which still retained its crystalline character, weighed 10.5 grams. It was therefore 10.5 per cent. of the meal and had the following composition:

FLAX-SEED GLOBULIN.—*Preparation* 1.

		Ash-free.
Carbon	51.29	51.42
Hydrogen	7.04	7.06
Nitrogen	18.57	18.61
Sulphur	0.76	0.76
Oxygen	..	22.15
Ash	0.25	..
		100.00

Ash.—0.6412 gram substance, dried at 110° C., gave 0.0016 gram ash = 0.25 per cent.

Carbon and hydrogen.—0.3264 gram dried substance gave 0.6138 gram CO_2 = 51.29 per cent. C, and 0.2067 gram H_2O = 7.04 per cent. H.

Nitrogen.—0.3504 gram dried substance gave 53.95 cc. N at 15° C. (barometer 773.0 mm. at 23° C.) = 18.57 per cent.

Sulphur.—0.8655 gram dried substance gave 0.0478 gram $BaSO_4$ = 0.0066 gram S = 0.76 per cent.

The filtrate from 1 was further dialysed for five days and, by proceeding in the manner just described, 0.4 gram of preparation 2 was obtained in the form of spheroids which, without correction for ash, yielded 18.74 per cent. of nitrogen.

FLAX-SEED GLOBULIN.—*Preparation* 2.

Nitrogen	18.74

Nitrogen.—0.2620 gram substance, dried at 110° C., gave 41.22 cc. N at 13° C. (barometer 758.5 mm. at 25° C.) = 18.74 per cent.

2. *Extraction with pure water at* 40° *C.*—40 grams of flaxseed meal containing 8.56 per cent. of nitrogen were treated with 200 cc. of distilled water at 40° for 5 hours. The solution was then made up to a liter and allowed to stand over-night at the temperature of the room. The extract was filtered off and, after washing the residue with water, was saturated with ammonium sulphate. The precipitate formed was filtered and the filtrate

very carefully tested for proteids with the biuret test, but none were found. The ammonium sulphate precipitate was dissolved in water and a little sodium chloride solution and, after removing a small insoluble residue by filtration, the clear solution was placed in a dialyser. After five days this solution was found to be free from chlorides and contained a deposit consisting of crystals and spheroids. After washing the latter with alcohol and ether and drying over sulphuric acid, it weighed 4 grams, being 10 per cent. of the flax-seed meal employed.

FLAX-SEED GLOBULIN.—*Preparation* 3.

		Ash-free.
Carbon	51.47	51.69
Hydrogen	..	..
Nitrogen	18.62	18.70
Sulphur	0.73	0.73
Oxygen	..	..
Ash	0.43	..

Ash.—0.5134 gram substance, dried at 110° C., gave 0.0022 gram ash = 0.43 per cent.

Carbon and hydrogen.—0.3535 gram dried substance gave 0.6672 gram CO_2 = 51.47 per cent. C; hydrogen was lost.

Nitrogen.—0.3107 gram dried substance gave 47.49 cc. N at 11.5° C. (barometer 771.5 mm. at 22° C.) = 18.62 per cent.

Sulphur.—0.7610 gram dried substance gave 0.0404 gram $BaSO_4$ = 0.056 gram S = 0.73 per cent.

3. *Extraction with sodium chloride solution after exhausting with water at* 20° *C.*—The residue of the flax-seed meal after extracting with cold water, as described, was next treated twice with 10-per cent. sodium chloride solution, the extract filtered clear and saturated with ammonium sulphate. The precipitate so produced was filtered off, removed from the paper, dissolved in 10-per cent. sodium chloride brine, filtered from a small insoluble residue and the clear solution dialysed. After 24 hours dialysis crystals and spheroids appeared, and after five days the solution was filtered from the precipitate, which was then washed with water, alcohol—at first dilute and afterwards absolute—and finally with ether, and dried over sulphuric acid. It weighed 2 grams and agreed quite well in composition with preparation 1, as may be seen from the following analysis:

FLAX-SEED GLOBULIN.—*Preparation* 4.

		Ash-free.
Carbon	50.92	51.17
Hydrogen	6.87	6.90
Nitrogen	18.86	18.95
Sulphur	0.88	0.88
Oxygen	..	22.10
Ash	0.49	..
		100.00

Ash.—0.5492 gram substance, dried at 110° C., gave 0.0027 gram ash = 0.49 per cent.

Carbon and hydrogen.—0.3105 gram dried substance gave 0.5797 gram CO_2 = 50.92 per cent. C, and 0.1921 gram H_2O = 6.87 per cent. H.

Nitrogen.—0.3791 gram dried substance gave 59.1 cc. N at 13° C. (barometer 771.0 mm. at 27° C.) = 18.86 per cent.

Sulphur.—0.4030 gram dried substance gave 0.0261 gram $BaSO_4$ = 0.0036 gram S = 0.88 per cent.

4. *Extraction with sodium chloride solution after extracting with water at* 40° *C.*—The residue of flax-seed meal, after extracting with water at 40°, as described on page 12, was twice treated with 10-per cent. sodium chloride brine and the clear, filtered extracts dialysed free from chlorides. A perfectly crystallised preparation resulted, which, when treated in the usual manner, weighed 2.7 grams, equal to 6.8 per cent. of the flax-seed meal. Dried at 110° and analysed, the following results were obtained:

FLAX-SEED GLOBULIN.—*Preparation* 5.

		Ash-free.
Carbon	50.79	51.46
Hydrogen	6.85	6.94
Nitrogen	18.17	18.41
Sulphur	0.89	0.90
Oxygen	..	22.29
Ash	1.30	..
		100.00

Ash.—0.6355 gram substance, dried at 110° C., gave 0.0083 gram ash = 1.30 per cent.

Carbon and hydrogen.—0.3865 gram dried substance gave 0.7197 gram CO_2 = 50.79 per cent. C, and 0.2382 gram H_2O = 6.85 per cent. H.

Nitrogen.—0.3824 gram dried substance gave 57.15 cc. N at 11.5° C. (barometer 770 mm. at 22° C.) = 18.17 per cent.

Sulphur.—0.6527 gram dried substance gave 0.0425 gram $BaSO_4$ = 0.0058 gram S = 0.89 per cent.

5. *Direct extraction with sodium chloride solution.*—100 grams of the flax-seed meal were extracted three successive times with 20-per cent. sodium chloride solution, and the clear, filtered, bright-yellow extracts were united and saturated with ammonium sulphate. The precipitate produced was filtered off, removed from the paper and dissolved in 10-per cent. sodium chloride brine, and this solution, after filtering from an insoluble residue, was submitted to dialysis. After five days the solution, free from chlorides, was filtered from the separated globulins and returned to the dialyser. The precipitate was treated in the same manner as in the preceding. It amounted to 11.65 per cent. of the flax-seed meal when dried over sulphuric acid, still retained its crystalline form and had the following composition:

FLAX SEED GLOBULIN.—*Preparation* 6.

		Ash-free.
Carbon	51.22	51.32
Hydrogen	6.85	6.87
Nitrogen	18.57	18.60
Sulphur	0.82	0.82
Oxygen	..	22.39
Ash	0.20	..
		100.00

Ash.—0.8020 gram substance, dried at 110° C., gave 0.0016 gram ash = 0.20 per cent.

Carbon and hydrogen.—0.4535 gram dried substance gave 0.8517 gram CO_2 = 51.22 per cent. C, and 0.2796 gram H_2O = 6.85 per cent. H.

Nitrogen.—0.3786 gram dried substance gave 58.33 cc. N at 15° C. (barometer 772.7 mm. at 23° C.) = 18.57 per cent.

Sulphur.—1.0265 grams dried substance gave 0.0612 gram $BaSO_4$ = 0.0084 gram S = 0.82 per cent.

The filtrate from this precipitate yielded only an insignificant amount of substance on further dialysis.

6. *Direct extraction with a saturated sodium chloride solution.*—As saturation of the sodium chloride extract of flax-seed meal with salt precipitated nearly all of the coagulable proteids, a preparation of the globulin was made by extracting 40 grams of the meal with a saturated brine and submitting the clear filtered extract to dialysis until all the salt was removed and the globulin was deposited in the dialyser in the form of spheroids. This deposit was filtered off, washed with water, alcohol and ether, and found to weigh 3.7 grams, being 9.25 per cent. of the meal. Dried at 110°, it had the following composition:

FLAX-SEED GLOBULIN.—*Preparation* 7.

		Ash-free.
Carbon	51.12	51.59
Hydrogen	7.21	7.27
Nitrogen	18.17	18.34
Sulphur	..	22.80
Oxygen	..	
Ash	0.92	..
		100.00

Ash.—0.5977 gram substance, dried at 110° C., gave 0.0055 gram ash = 0.92 per cent.

Carbon and hydrogen.—0.3985 gram dried substance gave 0.7478 gram CO_2 = 51.12 per cent. C, and 0.2587 gram H_2O = 7.21 per cent. H.

Nitrogen.—0.2407 gram dried substance gave 35.83 cc. N at 7° C. (barometer 760.6 mm. at 23° C.) = 18.17 per cent.

7. *The globulin extracted by direct treatment of the flax-seed meal with dilute potash solution.* (*a*) *Deportment of the globulin toward $\frac{2}{10}$ per cent. potash solution.*—It was necessary before extracting the meal with potash solution to determine, if possible, whether this reagent would alter the properties and composition of the globulin. Five grams of preparation 6 were dissolved in 25 cc. of $\frac{2}{10}$ per cent. caustic potash solution and the perfectly clear but somewhat brownish-colored liquid was diluted with 375 cc. of distilled water. A nearly colorless solution resulted, which was very carefully neutralised with extremely dilute hydrochloric acid. This threw down a snow-white precipitate soluble in the most minute excess of either acid or alkali, as well as in solutions of sodium chloride. A dilute warm solution of sodium chloride saturated with this precipitate and filtered from the excess of substance deposited the globulin, on cooling, in well-formed octahedral crystals. The remainder of the precipitate was washed with water, alcohol and ether, and, after drying over sulphuric acid, weighed 4.05 grams and had the following composition:

FLAX-SEED GLOBULIN.—*Preparation* 8.

		Ash-free.	Average of Preps. 1–10.
Carbon	51.52	51.67	51.48
Hydrogen	6.90	6.92	6.94
Nitrogen	18.74	18.79	18.60
Sulphur	0.82	0.82	0.81
Oxygen	..	21.80	22.17
Ash	0.26	..	..
		100.00	100.00

Ash.—0.7344 gram substance, dried at 110° C., gave 0.0019 gram ash = 0.26 per cent.

Carbon and hydrogen.—0.3403 gram dried substance gave 0.6428 gram $CO_2 = 51.52$ per cent. C, and 0.2115 gram $H_2O = 6.90$ per cent. H.

Nitrogen.—0.3294 gram dried substance gave 50.94 cc. N at 11.5° C. (barometer 766.7 mm. at 20° C.) = 18.74 per cent.

Sulphur.—0.6945 gram dried substance gave 0.0415 gram $BaSO_4 = 0.0015$ gram S = 0.82 per cent.

It is thus seen that this globulin retained its properties unchanged, without conversion into "alkali-albuminate," by solution in weak caustic potash. Its composition is in close agreement with the average of the preparations already described, the slight difference being most probably due to the greater purity of the recrystallised globulin. Grübler also obtained crystalline preparations from the globulin of the squash-seed after solution in weak potash-water.

Ritthausen has been severely criticised by physiological chemists because he used dilute caustic alkalies in extracting proteids, although he proved in many cases that the products thus prepared retained their solubility in sodium chloride solution and had the same composition as the globulins extracted directly by sodium chloride brine and precipitated therefrom by dilution.

(*b*) *Direct extraction of the flax-seed meal with dilute potash solution.*—11 grams of flax-seed meal were next treated directly with 55 cc. $\frac{2}{10}$-per cent. caustic potash solution and the mixture made up to 1100 cc. with distilled water. This solution had a distinct alkaline reaction toward litmus. After filtration 1000 cc. of the clear liquid, equal to an extract from 10 grams of substance, were saturated with ammonium sulphate, and the precipitate produced filtered off and dissolved as far as possible in sodium chloride brine. The resulting solution was filtered clear and dialysed until chlorides were removed. The substance separated by dialysis, under the microscope was seen to consist of spheroids and imperfectly developed crystals. The deposit filtered off, washed with water, alcohol and ether and dried over sulphuric acid weighed 1.75 grams, being 17.5 per cent. of the air dry flax-seed meal, or when both meal and globulin were dried at 110°, equal to 16.5 per cent. This substance had the following composition:

FLAX-SEED GLOBULIN.—*Preparation* 9.

Carbon	51.23	51.53
Hydrogen	6.90	6.94
Nitrogen	18.35	18.45
Sulphur	0.73	0.73
Oxygen	..	22.35
Ash	0.60	..
	0.60	100.00

Ash.—0.4839 gram substance, dried at 110° C., gave 0.0029 gram ash = 0.60 per cent.

Carbon and hydrogen.—0.3259 gram dried substance gave 0.6122 gram CO_2 = 51.23 per cent. C, and 0.2023 gram H_2O = 6.90 per cent. H.

Nitrogen.—0.3533 gram dried substance gave 53.15 cc. N at 11.5° C. (barometer 772. mm. at 21° C.) = 18.35 per cent.

Sulphur.—0.2751 gram dried substance gave 0.0152 gram $BaSO_4$ = 0.0021 gram S = 0.73 per cent.

Another preparation was made in nearly the same manner, as follows: 25 grams of flax-seed meal containing 8.64 per cent. of nitrogen were treated with 100 cc. of $\frac{2}{10}$-per cent. caustic potash solution and 700 cc. of distilled water added. The resulting mixture not being alkaline, 100 cc. more $\frac{2}{10}$-per cent. potash solution were added, imparting to the extract a distinct alkaline reaction. The solution was then filtered from the insoluble residue and the latter washed well with water. The filtrate and washings were united and saturated with ammonium sulphate. The precipitate obtained was then thoroughly extracted with 10-per cent. sodium chloride solution, and after filtering placed in a dialyser, where it remained two weeks. The deposit which formed consisted of spheroids. Filtered off and washed with alcohol and ether and dried over sulphuric acid, the product weighed 1.56 grams, being 6.2 per cent. of the meal taken. This substance was composed as follows:

FLAX-SEED GLOBULIN.—*Preparation* 10.

		Ash-free.
Carbon	51.28	51.50
Hydrogen	6.92	6.95
Nitrogen	18.29	18.37
Sulphur Oxygen	..	23.18
Ash	0.44	..
		100.00

Ash.—0.6730 gram substance, dried at 110° C., gave 0.0030 gram ash = 0.44 per cent.

Carbon and hydrogen.—0.2761 gram dried substance gave 0.5192 gram CO_2 = 51.28 per cent. C, and 0.1722 gram H_2O = 6.92 per cent. H.

Nitrogen.—0.3003 gram dried substance gave 46.27 cc. N at 10.5° C. (barometer 749. mm. at 22° C.) = 18.29 per cent.

The preceding analyses are here brought together for comparison.

Extracted by water at 20°.

	1	2	3
Carbon	51.42	..	51.69
Hydrogen	7.06	..	..
Nitrogen	18.61	18.74	18.70
Sulphur	0.76	..	0.73
Oxygen	22.15	..	.
	100.00		

Extracted by salt solution.

	After water at 20°. 4	After water at 40°. 5	Direct. 6	Direct. 7
Carbon	51.17	51.46	51.32	51.59
Hydrogen	6.90	6.94	6.87	7.27
Nitrogen	18.95	18.41	18.60	18.34
Sulphur	0.88	0.99	0.82	22.80
Oxygen	22.10	22.29	22.39	
	100 00	100.00	100.00	100.00

Extracted by $\frac{2}{10}$-per cent. potash solution.

	Prep. 6 dissolved in potash and precipitated. 8	9	10	Average. 1–10
Carbon	51.67	51.53	51.50	51.48
Hydrogen	6.92	6.94	6.95	6.94
Nitrogen	18.79	18.45	18.37	18.60
Sulphur	0.82	0.73	23.18	0.81
Oxygen	21.80	22.35		22.17
	100.00	100.00	100.00	100.00

These results agree so closely with the analyses of the globulin obtained from squash-seed that there can be no doubt that the two proteids are identical. This agreement is shown by the following figures:

	Flax.	Squash-seed.		
	Osborne.	Chittenden and Hartwell.[1]	Ritthausen.[2]	Grübler.[3]
Carbon	51.48	51.60	51.61	51.48
Hydrogen	6.94	6.97	7.00	6.76
Nitrogen	18.60	18.80	..	18.14
Sulphur	0.81	1.01	..	0.96
Oxygen	22.17	21.62	..	22.66
	100.00	100.00		100.00

III.—THE "ALBUMINATE" DERIVED FROM THE GLOBULIN.

In several cases where the ammonium-sulphate precipitate was treated with sodium chloride solution so long as anything was removed, there remained a considerable amount of undissolved proteid—evidently an "albuminate" derived from the globulin. When this substance was dissolved in dilute sodium carbonate solution and precipitated on neutralisation, a precipitate was obtained, which, on filtering off and washing with water, alcohol and ether, was analysed after drying at 110°. The composition of the various products thus obtained was very varied; in some cases being the same as that of the globulin, and in others quite different, especially in respect to nitrogen. It is then evident that, by the methods employed in making some of these preparations for analysis, great changes in the proteid were caused.

1. *The "Albuminate" dissolved in Sodium Carbonate Solution and precipitated on Neutralisation with Acid.*

When the ammonium-sulphate precipitate of the 10-per cent. sodium chloride extract from which preparation 4 was taken, was treated with brine, a portion remained undissolved. This was washed with 10-per cent. sodium chloride brine, dissolved in ½-per cent. sodium carbonate solution, precipitated by careful neutralisation with hydrochloric acid, the precipitate filtered off, washed with water, alcohol and ether, and dried over sulphuric acid. This substance weighed 0.6 gram and was the insoluble, or "albuminate," form of the globulin. It contained the following amount of nitrogen:

FLAX-SEED PROTEID.—*Preparation* **II.**

		Ash-free.
Nitrogen	18.63	18.84
Ash	1.14	..

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[1] J. Physiol. **11**, 440.
[2] J. prakt. Chem. **25**, 136.
[3] J. prakt. Chem. **44**, 369.

Ash.—0.3145 gram substance, dried at 110° C., gave 0.0036 gram ash = 1.14 per cent.

Nitrogen.—0.2478 gram dried substance gave 38.22 cc. N at 13° C. (barometer 769.5 mm. at 26° C.) = 18.63 per cent.

When the ammonium-sulphate precipitate from which preparation 6 was obtained was extracted with 10-per cent. sodium chloride solution, a considerable amount of proteid remained undissolved. This was then dissolved in ½-per cent. sodium carbonate solution and, after filtering clear, was precipitated on neutralisation with dilute hydrochloric acid. This precipitate, after washing with water, alcohol and ether, weighed, air dry, 4.4 grams and was marked Preparation **12**. It had the following composition:

FLAX-SEED PROTEID.—*Preparation* **12**.

			Ash-free.		
	I.	II.	I.	II.	Average.
Carbon	51.29	51.14	51.56	51.41	51.49
Hydrogen	7.16	6.98	7.19	7.01	7.10
Nitrogen	17.21	16.95	17.30	17.04	17.17
Sulphur	1.03	..	1.04	..	1.04
Oxygen	..	..	22.91	..	23.20
Ash	0.53	..	..	..	..
			100.00		100.00

Ash.—0.6587 gram substance, dried at 110° C., gave 0.0035 gram ash = 0.53 per cent.

Carbon and hydrogen, I.—0.3580 gram dried substance gave 0.6733 gram CO_2 = 51.29 per cent. C, and 0.2317 gram H_2O = 7.16 per cent. H.

II.—0.3391 gram dried substance gave 0.6357 gram CO_2 = 51.14 per cent. C, and 0.2128 gram H_2O = 6.98 per cent. H.

Nitrogen, I (Dumas' method).—0.3900 gram dried substance gave 55.36 cc. N at 13° C. (barometer 772.0 mm. at 26° C.) = 17.21 per cent.

II (Kjeldahl method).—0.8312 gram dried substance gave ammonia = 17.15 cc. HCl solution (1 cc. = 0.00822 gram N) = 16.95 per cent. N.

Sulphur.—0.5507 gram dried substance gave 0.0428 gram $BaSO_4$ = 0.0059 gram S = 1.03 per cent.

In another extraction the ammonium-sulphate precipitate, when thoroughly washed with 10-per cent. brine, left a considerable insoluble residue. This was dissolved in 1-per cent. sodium carbonate solution and, after filtering clear, was divided into two parts. One part was precipitated on adding very dilute hydrochloric acid to slightly acid reaction; the precipitate was filtered off and washed with water. After washing out the salts the precipitate began to dissolve. It was then washed with alcohol and ether. On drying at 110° it was found to have the following composition:

FLAX-SEED PROTEID.—*Preparation* 13.

			Ash-free.		
	I.	II.	I.	II.	Average.
Carbon	50.69	50.66	51.91	51.88	51.90
Hydrogen	6.58	6.59	6.74	6.73	6.74
Nitrogen	11.26	11.36	11.83	11.73	11.78
Sulphur Oxygen	..	..	29.72	29.86	29.58
Ash	2.35	..	..	..	..
			100.00	100.00	100.00

Ash.—0.3994 gram substance, dried at 110° C., gave 0.0094 gram ash = 2.35 per cent.

Carbon and hydrogen, I.—0.3570 gram dried substance gave 0.6635 gram $CO_2 =$ 50.69 per cent. C, and 0.2110 gram $H_2O =$ 6.58 per cent. H.

II.—0.3994 gram dried substance gave 0.7418 gram $CO_2 =$ 50.66 per cent. C, and 0.2375 gram $H_2O =$ 6.59 per cent. H.

Nitrogen, I.—0.3187 gram dried substance gave 31.22 cc. N at 17° C. (barometer 755.6 mm. at 20° C.) = 11.46 per cent.

II.—0.3193 gram dried substance gave 32.42 cc. N at 17° C. (barometer 755.6 mm. at 20° C.) = 11.56 per cent.

The other portion of the solution was saturated with ammonium sulphate, and carbon dioxide passed through it. But little precipitate being thus produced which could be removed by filtration, a very slight excess of hydrochloric acid was added, which caused a precipitate to fall. This was filtered off, washed thoroughly with water, alcohol and ether. On washing with water a little of the substance dissolved. Dried at 110°, the following results were obtained on analysis:

FLAX-SEED PROTEID.—*Preparation* 14.

			Ash-free.		
	I.	II.	I.	II.	Average.
Carbon	50.61	50.43	50.97	50.80	50.89
Hydrogen	6.87	6.71	6.92	6.76	6.84
Nitrogen	16.25	16.28	16.36	16.39	16.38
Oxygen Sulphur	..	..	25.75	26.05	25.89
Ash	0.71	..	..	..	..
			100.00	100.00	100.00

Ash.—0.4100 gram substance, dried at 110° C., gave 0.0029 gram ash = 0.71 per cent.

Carbon and hydrogen, I.—0.3482 gram dried substance gave 0.6462 gram CO_2 = 50.61 per cent. C, and 0.2154 gram H_2O = 6.87 per cent. H.

II.—0.3728 gram dried substance gave 0.6893 gram CO_2 = 50.43 per cent. C, and 0.2250 gram H_2O = 6.71 per cent. H.

Nitrogen, I.—0.3271 gram dried substance gave 46.1 cc. N at 17° C. (barometer 758.0 mm. at 21° C.) = 16.25 per cent.

II.—0.3479 gram dried substance gave 49.13 cc. N at 17° C. (barometer 758.0 mm. at 21 C.) = 16.28 per cent.

On a second time extracting with 10-per cent. sodium chloride solution the flax-seed meal from which the two preceding preparations had been obtained, and saturating this second extract with ammonium sulphate, it was found that a considerable part of the precipitate produced by the ammonium sulphate had become insoluble in 10-per cent. salt solution. After thoroughly washing with brine, the insoluble residue was dissolved in 1-per cent. sodium carbonate solution and the liquid filtered perfectly clear. This was then neutralised with the greatest care. When the precipitate separated from the solution and was apparently completely thrown down, it was found that the solution turned blue litmus paper quite red, but on drying the paper on carefully cleaned platinum it became blue again. On the other hand red litmus paper was unaffected by the solution until dried on platinum, when it became blue. This reaction was not due to the precipitate, for on filtering the solution perfectly clear the same result was obtained.

This filtrate was then carefully tested for further precipitable substance by adding extremely dilute hydrochloric acid, and also dilute sodium carbonate solution, but neither gave any more precipitate. Sodium chloride was also added to the filtrate in order to precipitate any acid-globulin present, but none was found. After washing the precipitate with water it was found to dissolve. The whole was therefore dissolved in distilled water and a solution obtained which behaved exactly like a solution of the crystallised globulin in dilute acid, giving a precipitate, on adding a little sodium chloride, which did not dissolve in a larger amount of salt. The solution was dialysed until all chlorides were removed. It then separated in a gelatinous mass adhering to the parchment. This was scraped off, rinsed into a beaker and allowed to settle over-night. In the morning it had gathered in a mass at the bottom of the vessel. It was filtered off, washed with absolute alcohol which did not dehydrate it completely, then with ether, and dried over sulphuric acid, when it became horny and translucent. Dried at 110° it had the following composition:

FLAX-SEED PROTEID.—*Preparation* 15.

			Ash-free.		Average.
	I.	II.	I.	II.	
Carbon	51.75	51.50	51.81	51.56	51.69
Hydrogen	6.88	6.86	6.88	6.86	6.87
Nitrogen	17.42	..	17.44	..	17.44
Sulphur	0.81	..	0.81	..	0.81
Oxygen	..	..	23.06	..	23.19
Ash	0.12	..	..	..	..
			100.00		100.00

Ash.—0.8320 gram substance, dried at 110° C., gave 0.0010 gram ash = 0.12 per cent.

Carbon and hydrogen, I.—0.3823 gram dried substance gave 0.7255 gram CO_2 = 51.75 per cent. C, and 0.2365 gram H_2O = 6.88 per cent. H.

II.—0.3559 gram dried substance gave 0.6720 gram CO_2 = 51.50 per cent. C, and 0.2195 gram H_2O = 6.86 per cent. H.

Nitrogen.—0.4134 gram dried substance gave 62.66 cc. N at 17° C. (barometer 755.6 mm. at 20° C.) = 17.42 per cent.

Sulphur.—0.7860 gram dried substance gave 0.0464 gram $BaSO_4$ = 0.0064 gram S = 0.81 per cent.

Again, 200 grams of flax-seed meal were extracted with 10-per cent. sodium chloride solution, the clear extract saturated with ammonium sulphate and the precipitate thus obtained thoroughly exhausted with brine. The undissolved residue was then treated with ½-per cent. sodium carbonate solution, the solution filtered, neutralised with dilute hydrochloric acid, and the resulting precipitate filtered off, washed with alcohol and ether, and dried over sulphuric acid. It weighed 5.9 grams, and when dried at 110° gave the following results on analysis:

FLAX-SEED PROTEID.—*Preparation* 16.

		Ash-free.
Carbon	51.59	51.72
Hydrogen	6.80	6.82
Nitrogen	18.35	18.40
Sulphur	0.96	0.96
Oxygen	..	22.10
Ash	0.26	..
		100.00

Ash.—0.6091 gram substance, dried at 110° C., gave 0.0016 gram ash = 0.26 per cent.

Carbon and hydrogen.—0.4015 gram dried substance gave 0.7596 gram CO_2 = 51.59 per cent. C, and 0.2458 gram H_2O = 6.80 per cent. H.

Nitrogen.—0.3432 gram dried substance gave 51.76 cc. N at 11.5° C. (barometer 771.8 mm. at 24° C.) = 18.35 per cent.

Sulphur.—0.7000 gram dried substance gave 0.0495 gram $BaSO_4$ = 0.0067 gram S = 0.96 per cent.

200 grams of the flax-seed meal were treated with water, and the fine meal in suspension decanted from the gummy husks. Sodium chloride was then added to the aqueous extract, and the solution filtered clear. This solution was then saturated with ammonium sulphate, and the large precipitate filtered off, pressed between filter-papers in order to remove as much as possible of the adhering solution, and dissolved in 10-per cent. sodium chloride brine. A very considerable part of the substance was now found to be insoluble in sodium chloride solution. This was therefore filtered off, washed with brine to free it from the soluble globulin, and then with water. The substance so obtained was divided into two parts. One was dissolved in ½-per cent. sodium carbonate solution, the resulting liquid filtered clear and neutralised with $\frac{2}{10}$-per cent. hydrochloric acid. Before complete neutralisation the substance began to precipitate. After neutralising as exactly as possible, the precipitate was filtered off and washed with distilled water. After the salts present were removed the precipitate began to dissolve in water, showing the properties of an acid-globulin. The substance was then washed with alcohol and ether, and, dried over sulphuric acid, weighed 6.66 grams. Dried at 110°, the following results were obtained on analysis:

FLAX-SEED PROTEID.—*Preparation* 17.

		Ash-free.
Carbon	51.61	52.04
Hydrogen	6.80	6.85
Nitrogen	17.12	17.26
Sulphur	..	..
Oxygen	..	..
Ash	0.84	..

Ash.—0.5500 gram substance, dried at 110° C., gave 0.0046 gram ash = 0.84 per cent.

Carbon and hydrogen.—0.4277 gram dried substance gave 0.8094 gram CO_2 = 51.61 per cent. C, and 0.2618 gram H_2O = 6.80 per cent. H.

Nitrogen.—0.3854 gram dried substance gave 52.95 cc. N at 6° (barometer 773.6 mm. at 21° C.) = 17.12 per cent.

2. *Solution of the "Albuminate" in Warm Sodium Chloride Solution.*

The other portion of the insoluble proteid last described was treated with 10-per cent. sodium chloride solution heated to 50°, and was found to dissolve almost completely. On cooling, a considerable amount of substance separated, and was seen under the microscope to consist of octahedral crystals. This preparation was washed with water, alcohol and ether, and weighed, air-dry, 1.4 grams. Dried at 110° it had the following composition:

FLAX-SEED GLOBULIN.—*Preparation* **18.**

		Ash-free.
Carbon	50.98	51.14
Hydrogen	6.79	6.81
Nitrogen	18.24	18.30
Sulphur Oxygen	..	23.75
Ash	0.32	..
		100.00

Ash.—0.3687 gram substance, dried at 110° C., gave 0.0012 gram ash = 0.32 per cent.

Carbon and hydrogen.—0.4261 gram dried substance gave 0.7965 gram CO_2 = 50.98 per cent. C, and 0.2604 gram H_2O = 6.79 per cent. H.

Nitrogen.—0.3215 gram dried substance gave 46.87 cc. N at 5° C. (barometer 773.5 mm. at 19° C.) = 18.24 per cent.

The filtrate from preparation **18** was then dialysed till free from salt, and the crystalline deposit resulting was filtered off, washed with water, alcohol and ether. It weighed, air-dry, 2.1 grams, and had the following composition when dried at 110°:

FLAX-SEED GLOBULIN.—*Preparation* **19.**

		Ash-free.
Carbon	51.30	51.39
Hydrogen	6.90	6.91
Nitrogen	18.54	18.57
Sulphur Oxygen	..	25.13
Ash	0.19	..
		100.00

Ash.—0.3759 gram substance, dried at 110° C., gave 0.0007 gram ash = 0.19 per cent.

Carbon and hydrogen.—0.3858 gram dried substance gave 0.7258 gram CO_2 = 51.30 per cent. C, and 0.2395 gram H_2O = 6.90 per cent. H.

Nitrogen.—0.2866 gram dried substance gave 42.63 cc. N at 6° C. (barometer 773.6 mm. at 21° C.) = 18.54 per cent.

The table here given will facilitate a comparison of the preceding analyses:

	11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Carbon	..	51.49	51.90	50.89	51.69	51.72	52.04	51.14	51.39
Hydrogen	..	7.10	6.74	6.84	6.87	6.84	6.85	6.81	6.91
Nitrogen	18.84	17.17	11.78	16.38	17.44	18.40	17.26	18.30	18.57
Sulphur	..	1.04	29.58	25.89	0.81	..	..	23.75	..
Oxygen	..	23.20			23.19	..	..		
		100.00	100.00	100.00	100.00			100.00	

It is clear that many of the above analyses represent no definite substance and that, in most cases, by the treatment employed extensive changes, both in the properties and composition of the proteid, have been brought about. Preparations **13**, **14**, **15** and **17** had the properties of an acid-globulin, being insoluble in water containing a small amount of salts, and soluble in pure distilled water containing a trace of acid, and also in alcohol; whereas preparations **11**, **12** and **16** were undissolved by distilled water. Preparations **18** and **19** were in all respects like the original globulin, and show therefore that the so-called "*albuminate*" of Weyl is something very different from an *alkali-albuminate.*

These analyses also show that the insoluble form of the globulin is the same in composition as the globulin itself. What the real cause of the change in solubility may be is not clear, but it is not improbable that the globulins form compounds with water which are soluble in solutions of salts, and that when separated from solution these hydrates break down and an insoluble form results. Or it may be that the globulins form loose compounds with other substances in the solution, as, for instance, coloring matters or salts, and that on warming, these are broken up and the original globulin is restored. A like conversion of an insoluble into a soluble globulin was accomplished by the writer with the so-called albuminate similarly obtained from the sodium-chloride extract of the oat-kernel.[1]

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[1] This Journal **14**, 212.

IV.—The Proteids remaining in Solution after removing the Globulin.

After separating the globulin by dialysis and filtration, the clear liquid can be heated to boiling without producing a coagulum, but if concentrated to a small volume a coagulation gradually takes place. If the dialysed liquid be treated with about 2 per cent. of sodium chloride, and a little hydrochloric acid be added, a precipitate is produced consisting of a proteid resembling an albumin in its solubility in water, but like a globulin in that, when precipitated by salt and acid, it forms an acid compound soluble in water nearly or wholly free from salts. On the other hand it is thrown out of such solutions upon neutralisation with sodium carbonate.

Similar substances were found in the extracts of the maize kernel and, in a paper on the proteids of that seed, were described as albumins.[1] Together with this body there is precipitated more or less proteose, resembling closely in composition the deutero-vittelose obtained by Chittenden and Hartwell from the crystallised proteid of the squash-seed.[2] After separating the coagulable proteids by concentrating their solution to a small volume and by filtration, there was always found in the filtrate more or less proteid matter of the character of the proteoses and peptones.

1. *Proteids coagulating on boiling.*

Two extractions were made, each with 100 grams of flax-seed meal; one (portion A) was treated with water, and the other (B) with 20-per cent. sodium chloride solution. Both these extracts were precipitated by saturating with ammonium sulphate, dissolving the precipitates in water containing sodium chloride, and dialysing until no more globulin was precipitated. Especial care was taken to make the separation of globulin as complete as possible, by the use of river-water remarkably free from dissolved salts. The clear solutions, free from globulin, were then concentrated by boiling and filtered from coagulum.

These preparations were washed with water, alcohol and ether, and dried at 110° C.; that from A, preparation **20**, weighed 0.8 gram and contained, ash-free, 17.75 per cent. of nitrogen, while that from B, preparation **21**, weighed 0.96 gram and contained 17.61 per cent.

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[1] This Journal **13**, 453, 529; **14**, 20.

[2] J. Physiology **11**, 435.

Another preparation was made by extracting 25 grams of flax-seed meal with very dilute potash-water, precipitating the proteids by saturation with ammonium sulphate, dissolving the precipitate in brine, dialysing the solution until the globulins had been separated, and concentrating the filtered liquid by boiling to small volume. The coagulum so produced was filtered off, washed with water, alcohol and ether, and dried at 110°. It weighed 0.3 gram, being 1.25 per cent. of the meal. It contained, without correction for ash, 17.65 per cent. of nitrogen—Preparation 22.

The close agreement in nitrogen between these three preparations indicates a common origin. The proteid precipitated with salt and acid, next to be described, contained about the same proportion of nitrogen and is unquestionably the substance yielding the coagulum on long-continued heating.

2. *Proteids precipitated by Sodium Chloride and Hydrochloric Acid.*

The extract obtained by treating 200 grams of flax-seed meal with 10-per cent. sodium chloride solution, saturating with ammonium sulphate and dialysing the aqueous solution of the precipitate, so obtained, until free from globulin, was treated with sodium chloride until it contained 2 per cent. of the salt. 300 cc. of $\frac{2}{10}$-per cent. hydrochloric acid were then added, and the large precipitate produced filtered off, suspended in 500 cc. of water, and 75 cc. of $\frac{2}{10}$-per cent. hydrochloric acid added. This dissolved a part of the precipitate. The solution was then filtered from the residue, which was washed with alcohol of gradually increased strength up to absolute, then with ether, and finally dried over sulphuric acid. This preparation 23 weighed 6.7 grams and, dried at 110°, contained, ash-free, 17.85 per cent. of nitrogen. Before drying, it was soluble in distilled water, imparting to the solution (which was not coagulated by boiling) a strong acid reaction. Upon neutralising this solution with sodium carbonate, the substance was thrown down in a form insoluble in sodium chloride solution. Addition of salt to the solution gave a precipitate, but nothing separated on adding three volumes of strong alcohol. All these reactions are characteristic of vegetable globulins when dissolved in very dilute acids.

The entire preparation was then dissolved in $\frac{2}{10}$-per cent. hydrochloric acid, and the resulting solution precipitated by carefully neutralising with sodium carbonate. This reprecipitation was made in order to separate any proteose which might possibly be mixed with the substance. The precipitate was then washed with water, alcohol and ether, and dried at 110°. Its composition was the following:

FLAX-SEED PROTEID.—*Preparation* 23.

			Ash-free.		
	I.	II.	I.	II.	Average.
Carbon	50.01	50.24	50.03	50.26	50.14
Hydrogen	6.70	6.74	6.70	6.74	6.72
Nitrogen	17.49	17.57	17.50	17.5	17.54
Sulphur Oxygen	..	..	..	..	25.70
Ash	0.04	..	..	..	..
					100.00

Ash.—0.4436 gram substance, dried at 110° C., gave 0.0002 gram ash = 0.04 per cent.

Carbon and hydrogen, I.—0.5433 gram dried substance gave 0.9963 gram CO_2 = 50.01 per cent. C, and 0.3277 gram H_2O = 6.70 per cent. H.

II.—0.3428 gram dried substance gave 0.6316 gram CO_2 = 50.24 per cent. C, and 0.2080 gram H_2O = 6.74 per cent. H.

Nitrogen, I.—0.3766 gram dried substance gave 53.15 cc. N at 5° (barometer 766.7 mm. at 20° C.) = 17.49 per cent.

II.—0.3159 gram dried substance gave 45.86 cc. N at 6° (barometer 751.0 mm. at 19° C.) = 17.57 per cent.

Preparation 23, as just described, after its first precipitation from the dialysed solution by salt and acid, was washed with very dilute hydrochloric acid in which some of it dissolved. These washings were then neutralised with a dilute solution of sodium carbonate, and the precipitate produced filtered off. After washing with water, alcohol and ether, and drying at 110° C., it weighed 1.0 gram—Preparation 24. Ash-free, it contained 17.80 per cent. of nitrogen.

It is evident that this substance has the same amount of nitrogen as the coagulated proteid derived from similar solutions. To facilitate comparison the analyses are here brought together:

	Prep. 20.	Prep. 21.	Prep. 22.	Prep. 23.	Prep. 24.
C	..	..	..	50.14	..
H	..	..	..	6.72	..
N	17.75	17.61	17.65	17.54	17.80

3. *The Proteoses and Peptones.*

The filtrate from preparation **24** was neutralised and then dialysed till free from chlorides, evaporated to very small volume and precipitated with alcohol. After washing with ether and drying over sulphuric acid, the precipitate weighed 1.04 grams —Preparation **25**. This substance had all the properties of a proteose. It dissolved instantly in pure water, was entirely uncoagulable, was precipitated by hydrochloric acid from a solution containing much sodium chloride, and gave a clear pink biuret-reaction. In composition it closely resembles deutero-vitellose, obtained by Chittenden and Hartwell by digestion of crystallised vitellin from the squash-seed with pepsin-hydrochloric acid. Its composition is shown by the following figures, together with that of the deutero-vitellose;

FLAX-SEED PROTEOSE.—*Preparation* **25**.

		Ash-free.	Deutero-vitellose.	
			I.	II.
Carbon	49.08	49.98	50.42	49.27
Hydrogen	6.83	6.95	6.74	6.70
Nitrogen	18.44	18.78	18.43	18.78
Sulphur Oxygen	..	24.29	24.41	25.25
Ash	1.80	..	..	..
		100.00	100.00	100.00

Ash.—0.3772 gram substance, dried at 110° C., gave 0.0068 gram ash = 1.80 per cent.

Carbon and hydrogen.—0.3683 gram dried substance gave 0.6628 gram $CO_2 = 49.08$ per cent. C, and 0.2263 gram $H_2O = 6.83$ per cent. H.

Nitrogen.—0.3500 gram dried substance gave 52.35 cc. N at 11.5° C. (barometer 780.4 mm. at 22° C.) = 18.44 per cent.

The filtrate from preparation **23**, which had been obtained by adding 2 per cent. of sodium chloride and some hydrochloric acid to the dialysed extract freed from the globulins, was next saturated with sodium chloride and a small precipitate obtained. This was filtered off, dissolved in water, the solution dialysed until free from chlorides, evaporated to small volume, precipitated with alcohol, washed with ether and dried over sulphuric acid. 0.80 gram of proteose was thus obtained. When dried at 110° it contained, ash-free, 18.33 per cent. of nitrogen—Preparation **26**.

The solutions freed from globulin by dialysis and from coagulable bodies by concentration, were in all cases found to contain a considerable amount of proteid matter having the properties of a mixture of proteoses and peptones. This mixed substance was very readily soluble in water to a solution which, when saturated with ammonium sulphate while hot, and filtered, gave a strong red biuret-reaction, and no precipitate with copper sulphate showing the presence of peptones. This was observed in all of the five preparations examined. The aqueous solution of the substance was precipitated by copper sulphate, gave a precipitate with nitric acid which dissolved on heating and reappeared on cooling, and a precipitate with ammonium sulphate. These reactions show the presence of proteoses.

THE PROTEIDS INSOLUBLE IN WATER AND SODIUM CHLORIDE SOLUTIONS.

After complete extraction with sodium chloride solution, more or less proteid was always found in the residue of the meal, most of which could be removed by treatment with $\frac{2}{10}$-per cent. potash solution. The amount of this substance was not large, in three cases being 1.30, 1.55 and 0.66 per cent., respectively. In no case were preparations obtained which appeared to be pure. The alkali extracted from the outer coating of the seed a large amount of coloring matter which on neutralisation was always precipitated with the proteid, imparting to the preparations a chocolate-brown color. The large amount of gum contained in the seed also rendered the preparation of these substances very difficult, as this gum was much more soluble in the alkaline liquid than in salt or acid solutions, and on neutralisation was undoubtedly carried down with the proteid. As a result no definite composition could be assigned to the substance so extracted. This result might be expected, even if the difficulties just mentioned did not exist, were the proteid substance still contained in the seed different in composition from the globulin; for this latter would necessarily be but imperfectly extracted by salt solutions, and would be taken up by the potash and precipitated on neutralisation. For these reasons the large number of preparations made and analysed gave very varying results and afforded no data for even an approximate statement of the composition of the proteid extracted. After complete exhaustion with $\frac{2}{10}$-per cent. potash solution, the extracted residue always contained a considerable amount of nitrogen, which may have escaped solution through protection afforded by the tissue of the seed, or it may have belonged to bodies insoluble in the reagents employed. No evidence on this point was obtained.

VI.—THE AMOUNT OF THE VARIOUS PROTEIDS SEPARATED FROM THE FLAX-SEED.

The results of this investigation, thus far recorded, show that the extracts of the flax-seed contain a globulin precipitable by dialysis; a proteid, resembling both globulin and albumin, precipitable by long-continued heating at 100°, as well as by sodium chloride in the presence of acid; proteose and peptone-like bodies, and a proteid not extracted by sodium chloride solution, but soluble in dilute potash-water.

All attempts to determine the amount of these various substances failed because of change, while in solution, into non-proteid bodies. It was further found that the relative amount of the various proteids was very variable; it is almost certain that the more soluble forms were largely, if not wholly, derived from the globulin in consequence of alteration during extraction and separation. These operations were in all cases greatly prolonged on account of the gum contained in the seed, which rendered filtration extremely difficult and slow. Putrefaction, however, was entirely prevented by the use of thymol. Numerous attempts were made to determine the total proteid-nitrogen in the seed, but in no case did the nitrogen extracted and recovered in the proteid precipitates, added to that in the extracted residue, equal the total nitrogen contained in the flax-seed meal.

This may be illustrated by the following figures: Two portions of 100 grams of flax-seed meal containing 8.40 per cent. of nitrogen were extracted,—A, first with water, then with 10-per cent. sodium chloride solution and, finally, with $\frac{2}{10}$-per cent. potash-water. B, first with 10-per cent. sodium chloride solution and then with $\frac{2}{10}$-per cent. potash-water. The amounts of proteid obtained, together with the nitrogen of each, were as follows, in per cent. of the meal:

	A.		B.	
	Proteid.	Nitrogen.	Proteid.	Nitrogen.
Total globulin	13.5	2.5139	16.05	2.9206
Potash extracted	1.3	0.1808	1.55	0.2305
Coagulum	0.8	0.1406	0.96	0.1674
Proteose	3.7	0.5872	1.30	0.1648
Total	19.3	3.4225	19.86	3.4833
Nitrogen in insoluble residue		0.4255		0.4556
Total accounted for		3.8480		3.9388
Nitrogen lost		4.5520		4.4612
		8.4000		8.4000

These two extractions were made at the same time and under the same conditions, and the results are in striking agreement. In extraction A, 0.4255 gram of nitrogen out of 8.4 grams of total nitrogen remained in the residue of the seed, showing that 94.94 per cent. of the total nitrogen was soluble in the reagents employed. The nitrogen extracted by potash-water amounted to 2.15 per cent. of the total, so that by water and by sodium chloride solution 92.79 per cent. of the total nitrogen was extracted. The nitrogen recovered from these solutions amounted to 38.59 per cent. of the total, so that the nitrogen lost equaled 4.5528 grams, or 54.2 per cent. This loss must have been due either to the presence of non-proteid nitrogenous substances, or to a decomposition of the proteid matter into diffusible nitrogen-containing compounds.

Numerous attempts were made to determine the total amount of proteid-nitrogen, with, however, very varying results. In one case 20 grams of flax-seed meal (=16.74 grams dried at 110° C.) were extracted with $\frac{2}{10}$-per cent. potash solution, the extract filtered, and neutralised with $\frac{2}{10}$-per cent. hydrochloric acid. The neutralisation-precipitate was filtered off, washed with water, alcohol and ether and dried at 110°. It weighed 5.4815 grams (=32.74 per cent. of the meal taken), and contained 0.9176 gram nitrogen—equivalent to 63.44 per cent. of the total nitrogen of the meal. The insoluble residue of the meal contained 0.2486 gram nitrogen=17.19 per cent. The nitrogen accounted for was in this case 80.53 per cent. of the total.

In another experiment 50 grams of flax-seed meal were extracted with 1000 cc. of 20-per cent. brine and filtered as rapidly as possible. 500 cc. of the extract (=25 grams of the flax-seed meal, or

20.925 grams dried at 110° C.) were then precipitated as completely as possible with dilute hydrochloric acid, and the resulting precipitate filtered off and washed with a dilute solution of sodium chloride containing a very little hydrochloric acid, then with alcohol and ether. Dried at 110° it weighed 5.7555 grams. This precipitate was therefore 27.50 per cent. of the meal taken and contained 0.8927 gram nitrogen=49.38 per cent. of the total nitrogen of the meal. The filtrate from this preparation was examined carefully for precipitable proteids, but no more could be obtained. After neutralising, the solution and washings were put in a dialyser and the salts separated. The solution was then evaporated to small volume and precipitated with absolute alcohol; the precipitate was washed with ether and dried at 110°. During the concentration a little coagulum was found, but this was not filtered off. In this way 2.36 grams of substance were obtained, having a large amount of ash. Ash-free, this substance formed 9.61 per cent. of the meal employed and contained 0.2294 gram of nitrogen=12.69 per cent. of the total nitrogen. The amount of nitrogen in these two preparations was 62.07 per cent. of the total. The nitrogen remaining in the meal after extraction was not determined on account of the very difficult filtration caused by the gum.

If this nitrogen is assumed to be the same as that contained in the residue extracted by potash, *i. e.* 17.19 per cent. of the total nitrogen, as described in the preceding experiment, the nitrogen accounted for would be 79.26 per cent. of the total. If we assume that in the first experiment the proteose present was equal to that found in the second, we should then account for 93.22 per cent. of the nitrogen. These experiments therefore indicate that the loss of nitrogen observed is due to a change in the proteids resulting in diffusible nitrogenous products.

To obtain further evidence on this point the seed was most carefully examined for other nitrogenous substances according to E. Schulze's method, but with negative results. It was, however, found that much non-proteid nitrogen occurred in the diffusate, and that the amount of nitrogen passing out of the dialyser in equal times was tolerably constant and therefore unquestionably due to a slow and uniform decomposition. This is shown by the following experiments:

100 grams of flax-seed meal suspended in 1500 cc. of distilled water were placed in a dialyser immersed in an equal volume of

distilled water. After 48 hours the diffusate was carefully tested without finding any proteid matter. The solution was then acidified with pure sulphuric acid, concentrated to small volume and the nitrogen present determined by Kjeldahl's method to be 0.1808 gram. This process was repeated six times, and at the conclusion of the experiment the contents of the dialyser were found to be wholly free from any odor or other evidence of putrefaction, having been protected by a liberal use of thymol. The amount of nitrogen found to have passed the parchment after each diffusion-period of 48 hours was as follows:

1st diffusate	0.1808 gram.
2d "	0.3077
3d "	0.2577
4th "	0.3445
5th "	0.3417
6th "	0.3042
Total nitrogen	1.7366

The fact that the nitrogen contained in the first diffusate was less than that in the others, and that the latter contained a nearly constant amount, is strong evidence that the diffusible nitrogenous substances did not exist ready-formed in the seed at the beginning of the experiment, but resulted from a slow decomposition of the proteid.

Several other trials of this character gave the same result, the diffusate in all cases being free from proteid matter, but containing bodies which evolved ammonia on heating with caustic alkalies. The nature of these substances was not discovered. It might naturally be supposed that this change was brought about through the action of a ferment similar to that contained in the pawpaw and the pineapple, but careful experiments with acid, alkaline and neutral extracts of the flax-seed proved it to be wholly free from any ferment capable of digesting coagulated egg-albumin, even after many hours contact at 40°.

Extraction of the flax-seed with water at 40° for some hours and subsequent exhaustion with 10-per cent. sodium chloride solution, gave no evidence of a proteolytic ferment, the yield of globulin under this treatment being unusually large. Extraction with a 20-per cent. solution of sodium chloride heated to 70°—whereby it was thought a ferment might be coagulated and rendered inoperative—yielded no more globulin than usual; in fact all attempts failed to disclose satisfactory evidence of the existence of a ferment.

It is to be noted that when the flax-seed meal was directly extracted with dilute potash-water, 32.74 per cent. of the meal was obtained in the form of a precipitated proteid when the solution was neutralised. The insoluble residue of the meal further yielded 0.2486 gram of nitrogen, which would be equivalent to 8.0 per cent. of proteid containing the amount of nitrogen found in the globulin, *viz.*, 18.6 per cent. The nitrogen of the neutralisation precipitate would be equivalent to 29.4 per cent. of globulin. The sum of these would be 37.4 per cent. of the meal.

The results of this investigation already given show that the globulin and the body extracted by dilute potash are the only proteids found in the extract which are precipitated from an alkaline solution on neutralisation. Therefore these two proteids must be the only ones contained in the precipitate. If we assume that the proteids in the flax-seed have, on the average, 18 per cent. of nitrogen, the meal extracted in this case would contain 48.0 per cent. of proteids. The 37.4 per cent. thus accounted for amounts to 78.0 per cent. of the total proteids.

In extract A (see page 656), by the same method of calculation, —*i. e.*, adding together the nitrogen of the insoluble residue, that of the potash-extract and of the globulin, and multiplying by 5.37 (the nitrogen-factor for a substance containing 18.6 per cent. of nitrogen)—we account for 16.75 per cent. of the meal, or only 36.3 per cent. of the total proteids. The difference between 78 per cent. (found in the potash extract) and 36.3 per cent. (in extract A) is 41.7 per cent.. which loss must clearly have been caused by a breaking up of the globulin or of the body extracted by potash-water. It has been shown (page 656) that in extract A 92.79 per cent. of the nitrogen was extracted by salt solution and water, and that more than two-thirds of the remaining 7.21 per cent. of nitrogen was contained in the residue and did not go into solution. It is clear, therefore, that the substance extracted by potash solution cannot be considered as the source of the loss. It is therefore certain that the globulin is the principal proteid suffering change.

As a confirmation of the idea that the crystallisable globulin suffers this loss, and also yields a large proportion of the water-soluble proteids, the results obtained by dialysing salt solutions of the globulin are important. 10 grams of air-dry crystallised globulin were dissolved in 10-per cent. sodium chloride solution and the clear filtered liquid placed in a dialyser. After complete removal of the chlorides the deposited globulin was filtered off, and the filtrate found to give a strong biuret-reaction and a precipitate with sodium chloride and acid.

In another case 17 grams of air-dry crystalline globulin were dissolved in 10-per cent. sodium chloride solution, the insoluble matter was filtered off and, after thorough washing with salt solution, water, alcohol and ether, was found to weigh 1.27 grams. The clear solution was dialysed free from chlorides in water of 6°, and filtered from the separated globulin. This, after washing with water, alcohol and ether, weighed, air-dry, 12.19 grams. The clear filtrate gave a biuret-reaction of a decided red tint, and on adding hydrochloric acid to its solution, saturated with sodium chloride, a precipitate. This solution was then concentrated and 0.11 gram of coagulum obtained. Filtered from this coagulum and precipitated with alcohol the solution gave 0.4 gram of proteose. It is thus evident that the salt solution of the globulin yields substances of the same character as those obtained from the extract of the seed. The percentage amount of these substances is shown by the following figures:

Globulin taken	17.00 grams	
Insoluble	1.27	
Dissolved globulin	15.73 grams	
Recovered "	13.46	85.460 per cent.
" coagulum	0.11	0.007
" proteose	0.40	0.028
Loss		14.505
		100.000

It is to be noted that these figures show a loss of 14.5 per cent. of proteid matter. This is far in excess of any mechanical loss which could have occurred, and can only be explained by a change in the proteid whereby diffusible substances were produced and, perhaps, also others not precipitable by strong alcohol. In either case substances other than proteid were formed. A similar loss of proteids was observed in all the extractions.

It has been shown that after separating the globulin as completely as possible by dialysis, there was found in the solution a body similar to albumin but having properties in common with globulin. The amount of this substance varied greatly, in some cases very little being found and in others large amounts. This was, unquestionably, for the most part, if not wholly, derived from the globulin, for in those extracts in which it occurred in the largest amount the globulin was found in greatly diminished quantity. A proteid having similar reactions was also found in the aqueous solution obtained by redissolving the globulin in sodium chloride brine and separating a second time by dialysis. Whether this substance exists in the seed in small quantities, or is wholly derived from the globulin during the process of extraction and separation, cannot be determined from the results of the present investigations.

In regard to the amount of proteoses and peptones the same must be said. It is pretty certain that the peptones are wholly formed during the extraction and separation, as no evidence of their presence in the extract when first made could be obtained. It is not possible, however, to detect minute quantities of peptones with certainty in strongly colored vegetable extracts rich in sugars.

It is exceedingly desirable to determine as accurately as possible the amount of each proteid contained in the seed, and to know exactly its nitrogen-content so that an accurate factor may be obtained for calculating the proportion of proteids from the nitrogen found.

It is evident from the preceding statements that it is impossible to say exactly what this factor should be for flax-seed, but a pretty close approximation can be made—one at least far more accurate than the factor at present in use based on a content of 16 per cent. of nitrogen. It has been shown on page 656 that about 93 per cent. of the nitrogen of the seed is extracted by salt solutions. This nitrogen has been shown to belong chiefly to the globulin which contains 18.6 per cent. of nitrogen. The albumin-like body was found to contain 17.7 per cent. of nitrogen, and the proteose prepared in a pure state contained in one case 18.78 per cent. and in another 18.33 per cent. of nitrogen. If, then, we assume the proteids to contain collectively an average of 18.00 per cent. of nitrogen we will not be very far from the truth. The factor then for flax-seed would be 5.55 instead of 6.25, and, for a sample of linseed meal containing 7 per cent. of nitrogen, would give a content of proteid of 38.85 per cent. instead of 43.75—a difference of very considerable magnitude.

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CRYSTALLISED VEGETABLE PROTEIDS.

By Thomas B. Osborne.

The existence of crystallised proteids in seeds was pointed out by Hartig in 1855. Four years later, Maschke obtained hexagonal plates of proteid matter by extracting Brazil-nuts with water heated to 40°–50° and evaporating the filtered extract at 40°. Nageli[1] investigated the crystal-like forms from the Brazil-nut as well as the artificially produced crystals of Maschke and concluded that they differed in some respects from true crystals. He therefore designated them as "crystalloids."

Sachsse,[2] following Maschke's method, and also by precipitating the aqueous extract with carbonic acid, obtained several preparations of proteid from the Brazil-nut which he analysed. These preparations were, however, not distinct crystals, but were composed of small discs.

Schmiedeberg[3] obtained crytallised products by treating the aqueous extract of the Brazil-nut with carbon dioxide, washing the precipitated proteid, digesting the precipitate with magnesia suspended in water at 35°, filtering and evaporating at the same temperature. These crystals he considered to be a compound of the proteid with magnesia.

Drechsel[4] obtained crystals, presumably hexagonal plates, by submitting the solution containing the "magnesia compound," prepared as Schmiedeberg suggested, to dialysis in a vessel containing alcohol.

Drechsel afterwards obtained finely developed crystals by allowing a warm sodium chloride solution saturated with the proteid of the Brazil-nut to cool slowly, when the substance separated in well-formed crystals.[5]

At Drechsel's suggestion Grübler applied this method with some modifications to the proteids of squash-seed, and made a large number of preparations of perfectly formed octahedral crystals whose properties and composition he described at length.[6]

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[1] Botanische Mittheilungen (München, 1863), Vol. I.

[2] Die Farbstoffe, Kohlenhydrate und Proteinsubstance (Leipzig, 1877), p. 315.

[3] Ztschr. physiol. Chem. **1**, 205.

[4] J. prakt. Chem. **19**, 331.

[5] Grübler : *cf. ibid.* **23**, 100.

[6] J. prakt. Chem. **23**, 97.

Ritthausen[1] obtained crystallised preparations from the castor-bean, hemp-seed and sesame-seed, which separated from a warm sodium chloride solution on cooling in the form of regular octahedrons. The composition and properties of the crystals obtained from the hemp-seed and castor-bean he described in a subsequent paper.[2]

The writer next prepared rhombohedral and octahedral crystals from the oat-kernel by cooling a warm dilute sodium chloride solution saturated with the proteid.[3]

The writer has also obtained octahedral crystals from flax-seed by extracting with a solution of sodium chloride and dialysing the filtered extract; the proteid separating in well-formed crystals as the salts were removed.[4]

The fact that these proteid substances can be artificially crystallised is not only interesting in itself, but is important as presumably furnishing a means for making preparations of undoubted purity which will afford a sure basis for further study of their properties. The contradictory statements made by the various investigators, not only in regard to properties and composition of these bodies but also in respect to the value of the methods of solution and separation which have been employed hitherto, render an exact knowledge of all the facts relating to these substances a matter of the highest scientific and practical importance.

An examination of the literature indicates that definitely crystallised preparations from the Brazil-nut have never been analysed, and also shows that the published analyses do not agree sufficiently to fix the composition of the substance.

Ritthausen's observations on the properties of the crystallised proteids of the hemp-seed and castor-bean indicate that they are closely related to, if not identical with, the body obtained by Grübler from the squash-seed; yet the results of Ritthausen's analyses differ widely from those first made by Grübler.

The composition of the crystallised proteid of the squash-seed has been fixed within narrower limits by the analyses of Chittenden and Hartwell,[5] Ritthausen,[6] and Grübler.[7] It seemed desirable, therefore, that the composition and properties of the various crystallised proteids should be investigated anew in order to determine the relations of these substances.

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[1] J. prakt. Chem. **23**, 481.

[2] *Ibid.* **25**, 130.

[3] Report Conn. Agri. Expt. Station 1890, and This Journal **13**, 408; **14**, 212.

[4] This Journal **14**, 329, 629.

[5] J. of Physiology **11**, 435.

[6] J. prakt. Chem. **25**, 137.

[7] *Ibid.* **44**, 369.

As the writer had already prepared crystallised products from the oat-kernel and flax-seed, he determined to reinvestigate the similar bodies obtainable from the Brazil-nut, hemp-seed, castor-bean and squash-seed, and the results of this investigation are embodied in the following pages.

CRYSTALLISED PROTEID OF THE BRAZIL-NUT, *Bertholletia.*

If a thin section of the meat of a Brazil-nut is examined under the microscope, after washing with ether and then with alcohol, a large number of bodies may be seen which more or less resemble crystals in form. If cold water is next applied to the section, an outer coating of these masses appears to be dissolved and a great number of apparently rhombohedral crystals are set free. These crystals are proteid in character, and on adding some sodium chloride solution dissolve instantly. If warm water is used instead of cold, the substance of these crystals dissolves, doubtless in the dilute saline solution which is formed with the alkali-salts of the seed, but which, when cold, has little, if any, solvent power. This view is supported by the fact that the proteid extracted from the seed is wholly insoluble in pure water, either cold or warmed to 40°.

Maschke,[1] as already stated, made a solution of this substance by extracting the oil-free meats with water and evaporating at 40°–50°. He thus obtained thick six-sided plates which he says "belong undoubtedly to the regular system, and the same form would be obtained if an octahedron were cut into three equal parts parallel to one of its octahedral faces; the middle part would then produce in every respect one of these six-sided plates."

Maschke made an analysis of his preparations, but considered that the substance was a compound of casein with an acid. Sachsse,[2] following Maschke's directions, failed to obtain crystals, the substance separating in small discs (*scheibchen*). He also obtained small discs by precipitating the aqueous extract with carbonic acid.

As a mean of five analyses of the preparations made after drying at 100°–110°, he gave the following:

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[1] J. prakt. Chem. **74**, 436.

[2] Die Farbstoffe, Kohlenhydrate und Proteinsubstance (Leipzig, 1877), p. 315.

CRYSTALLISED GLOBULIN OF BRAZIL-NUT.

BRAZIL-NUT GLOBULIN.—*Sachsse.*

	a. discs.
Carbon	51.00
Hydrogen	7.25
Nitrogen	18.06
Sulphur	1.36
Phosphoric acid (P_2O_5)	0.82
Oxygen	21.51
	100.00
Ash	0.76

The ash was determined by burning the substance mixed with calcium phosphate, and was found to equal in amount the phosphoric acid obtained by fusing with soda and potassium nitrate and precipitating with uranium acetate. Sachsse therefore concluded that the substance belonged to the class of vegetable caseins.

Th. Weyl,[1] in a paper on animal and vegetable proteids, published an analysis of the proteid of the Brazil-nut obtained by extracting the oil-free meats with 10-per cent. sodium chloride solution, precipitating by diluting and passing through the solution carbonic acid gas, washing the precipitate with water and then boiling with alcohol and drying.

He found the preparation thus made, after deducting the ash, to have the following composition:

BRAZIL-NUT GLOBULIN.—*Weyl.*

	b.
Carbon	52.43
Hydrogen	7.12
Nitrogen	18.10
Sulphur	0.55
Oxygen	21.80
	100.00

Weyl considered the substance to be a globulin resembling the vitellin obtained from the yolk of eggs.

Ritthausen,[2] replying to the criticisms of Weyl on the methods employed by him which involved the use of weak alkali solutions in preparing proteids from seeds, published the results obtained by extracting the oil-free meats of the Brazil-nut with a dilute solution of potash, precipitating the filtered extract with acetic acid, and washing the precipitate so produced with water, alcohol and ether. After drying at 130°, Ritthausen found his preparation to have the following composition:

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[1] Ztschr. physiol. Chem. **1**, 72.

[2] Pflüger's Archiv **16**, 301.

BRAZIL-NUT GLOBULIN.—*Ritthausen.*

	c.
Carbon	52.29
Hydrogen	7.24
Nitrogen	18.09
Sulphur	1.32
Oxygen	21.06
	100.00

The considerable discrepancies among the foregoing analyses and the fact that none of the preparations were distinctly crystallised make further investigations desirable. For this purpose a large quantity of fresh Brazil-nuts was procured, the outer shells removed, the perfectly sound meats were carefully selected, chopped fine and treated with benzine (petroleum-ether) in order to remove the oil. The finer portions of the material were then washed through a straining cloth by the aid of benzine, and a quantity of fine white meal was thus obtained.

100 grams of this meal were then treated with 10-per cent. sodium chloride solution and the very slightly colored extract filtered perfectly clear. The residue of the meal was treated twice more in the same way with sodium chloride solution, and the extracts obtained were united and saturated with pure ammonium sulphate. The snow-white precipitate resulting was thrown on a filter and, when freed from the solution, was removed from the paper and suspended in distilled water. The dilute solution of ammonium sulphate thus produced dissolved but a part of the precipitate. Complete solution resulted immediately on adding a little sodium chloride, showing that this latter salt is a far more energetic solvent for this substance than ammonium sulphate. The solution, after filtering perfectly clear, was placed in a dialyser and suspended in running water for three days, when it was removed and filtered from the large amount of separated substance. The solid product was washed thoroughly with water, alcohol and ether, and dried over sulphuric acid. It weighed nearly 25 grams. Under the microscope it was seen to consist wholly of crystals in the form of hexagonal plates, as shown in the accompanying plate. Dried at 110° these crystals had the following composition:

BRAZIL-NUT GLOBULIN: *Crystals—Preparation* 1.

	I.	II.	Average.	Ash-free.
Carbon	52.11	52.05	52.08	52.18
Hydrogen	6.91	6.92	6.92	6.92
Nitrogen	18.28	18.25	18.27	18.30
Sulphur	1.03	1.06	1.05	1.05
Oxygen	..	..	..	21.55
Ash	0.20	..	..	..
				100.00

Ash.—0.8475 gram substance, dried at 110°, gave 0.0017 gram ash=0.20 per cent.

Carbon and hydrogen, I.—0.3702 gram dried substance gave 0.7072 gram CO_2=52.11 per cent. C, and 0.2303 gram H_2O=6.91 per cent. H.

II.—0.3736 gram dried substance gave 0.7130 gram CO_2=52.05 per cent. C, and 0.2326 gram H_2O=6.92 per cent. H.

Nitrogen, I.—0.3887 gram dried substance gave 57.14 cc. N at 5° (barometer 769.5 mm. at 22°) = 18.28 per cent.

II.—0.3953 gram dried substance gave 57.74 cc. N at 5° (barometer 773.0 mm. at 22°) = 18.25 per cent.

Sulphur, I.—0.7940 gram dried substance gave 0.0596 gram $BaSO_4$ = 1.03 per cent. S.

II.—0.6020 gram dried substance gave 0.0465 gram $BaSO_4$ = 1.06 per cent. S.

A second preparation of this substance was made by extracting 50 grams of the oil-free meats with 10-per cent. sodium chloride solution and at once dialysing the clear filtered extract. During two days nothing solid appeared in the dialyser, but soon after a deposit began to form, and at the end of seven days a considerable precipitate had separated which was filtered off, washed with water, alcohol and ether, and when dried over sulphuric acid weighed 6 grams. Under the microscope this substance appeared to consist of small spheroids with a more or less irregular outline, strongly suggesting crystals, but presenting no definite crystalline form. Dried at 110°, the substance yielded the following results on analysis:

BRAZIL-NUT GLOBULIN: *Spheroids—Preparation* 2.

		Ash-free.
Carbon	51.87	52.35
Hydrogen	6.90	6.96
Nitrogen	18.00	18.16
Sulphur	1.11	1.12
Oxygen	..	21.41
Ash	0.92	..
		100.00

Ash.—0.6811 gram substance, dried at 110°, gave 0.0063 gram ash = 0.92 per cent.

Carbon and hydrogen.—0.2919 gram dried substance gave 0.5515 gram CO_2 = 51.87 per cent. C, and 0.1823 gram H_2O = 6.90 per cent. H.

Nitrogen.—0.3963 gram dried substance gave 57.14 cc. N at 5° (barometer 772.7 mm. at 23°) = 18.00 per cent.

Sulphur.—0.8100 gram dried substance gave 0.0648 gram $BaSO_4$ = 1.11 per cent. S.

A third preparation was made by extracting 25 grams of the oil-free meal with distilled water heated to 60°. The solution was then allowed to stand several days in a cold room at a temperature of about 5°, thymol being freely used to prevent decomposition. After the separated substance had settled, the supernatant solution was decanted, the sediment collected on a filter, washed with water, alcohol and ether, and dried over sulphuric acid. It weighed 7 grams. The particles composing this precipitate were similar to those of the preparation last described, but smaller. Dried at 110°, it was found by analysis to have the following composition:

BRAZIL-NUT GLOBULIN: *Spheroids—Preparation* 3.

		Ash-free.
Carbon	51.78	52.16
Hydrogen	6.93	6.98
Nitrogen	18.19	18.32
Sulphur	1.06	1.07
Oxygen	..	21.47
Ash	0.72	..
		100.00

Ash.—0.7667 gram substance, dried at 110°, gave 0.0055 gram ash = 0.72 per cent.

Carbon and hydrogen.—0.3252 gram dried substance gave 0.6174 gram CO_2 = 51.78 per cent. C, and 0.2030 gram H_2O = 6.93 per cent. H.

Nitrogen.—0.4062 gram dried substance gave 59.42 cc. N at 5° (barometer 769.5 mm. at 22°) = 18.19 per cent.

Sulphur.—0.8210 gram dried substance gave 0.0630 gram $BaSO_4$ = 1.06 per cent. S.

These analyses show that this proteid has the same composition whether crystallised or spheroidal, and that the different methods of extraction give the same results. To facilitate comparison, all the analyses are here tabulated.

BRAZIL-NUT GLOBULIN.

	Sachsse.[1]	Ritthausen.	Weyl.		Osborne.	
	a	*b*	*c*	1	2	3
	discs.			crystals.	spheroids.	spheroids.
Carbon	51.42	52.29	52.43	52.18	52.35	52.16
Hydrogen	7.31	7.24	7.12	6.92	6.96	6.98
Nitrogen	18.21	18.09	18.10	18.30	18.16	18.32
Sulphur	1.37	1.32	0.55	1.06	1.12	1.07
Oxygen	21.69	21.06	21.80	21.54	21.41	21.47
	100.00	100.00	100.00	100.00	100.00	100.00

With the exception of Sachsse's carbon determination, the figures for this element and for nitrogen are in fair agreement. The figures for hydrogen obtained by the writer are somewhat lower than the others, but as special precautions were taken to keep the reagents absolutely free from moisture, and as these agree with each other, it is probable that they are more nearly correct.

Weyl's sulphur determination is unquestionably incorrect. Sachsse and Ritthausen obtained about 0.2 per cent. more sulphur than the writer, but as it does not appear that either of these investigators examined the ash of their preparations for sulphate, it is possible that the cause of this difference may be due to sulphur present in such form. The writer's reagents were absolutely free from any trace of sulphur.

In view of these facts, and also since preparation 1 was well crystallised and in all probability pure, we may fairly take its analysis as closely representing the composition of the crystalline proteid of the Brazil-nut.

There can be little doubt that this artificially crystallised proteid is identical with that naturally occurring in the Brazil-nut, with which it agrees in its properties. The fact that it crystallises during dialysis is strong evidence that it is the same substance, entirely unchanged, for the "crystalloids" of the seed almost certainly were deposited in its cells by a similar process.

It is true that the artificial crystals are hexagonal plates, while the majority of the natural crystals resemble rhombohedrons, but the writer has shown that oat-globulin under a slight change of conditions may yield either octahedral or rhombohedral crystals. So the proteid of hemp-seed sometimes gives hexagonal plates, although as a rule octahedral crystals are obtained.

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[1] Sachsse's analysis is here calculated free from phosphoric acid.

The reactions of the artificially crystallised proteid of the Brazil-nut are as follows:

Insoluble in pure distilled water, even on warming to 50° C. Soluble in solutions of sodium chloride, from which it is partly precipitated on dilution with water, but not thrown down by saturation with sodium chloride. Precipitated completely by saturation with ammonium sulphate, and partially by saturation with magnesium sulphate. Very soluble in distilled water containing a minute amount of acid.

Water containing $\frac{2}{100}$ per cent. of hydrochloric acid dissolves the proteid at once; the amount of acid required being proportional to the quantity of substance. In other words, sufficient acid must be present to convert all the substance into an acid compound before complete solution results. Addition of a very small amount of sodium chloride, or other salt, precipitates the solution. This precipitate is insoluble in a large amount of sodium chloride, denoting the formation of an acid-compound. These acid solutions do not coagulate on boiling and are not precipitated by alcohol.

Citric acid dissolves the proteid less readily than hydrochloric acid, solutions of $\frac{1}{20}$ per cent. having but little solvent power. ½ per cent. solution of citric acid gives a turbid solution, which becomes clear at once on addition of a little sodium chloride, but is precipitated on adding more of the salt, the precipitate being insoluble in an excess.

Dilute sodium carbonate solutions of ½ to ¼ per cent. dissolve the proteid instantly and completely, as do also solutions containing a very little caustic alkali. On careful neutralisation the proteid is thrown down unchanged, being readily and completely soluble in sodium chloride solution. If acid is added in excess the proteid dissolves, and on again neutralising is precipitated in a form soluble in sodium chloride.

Dissolved in 10-per cent. sodium chloride solution a turbidity is produced on gradually heating to 70°, and on raising the heat to 86° flocks separate, which increase in amount if the temperature is slowly raised to 100°. This substance responds to all the usual tests for proteids, such as the biuret, Millon's, xanthoproteic, etc. The same reactions were given by the preparations made by cooling the warm aqueous extract. These reactions show this proteid to be a true globulin of the vitellin class.

CRYSTALLISED PROTEID OF HEMP-SEED.

As already stated, Ritthausen has described[1] a crystalline preparation obtained by extracting powdered hemp-cake with 5-per cent. sodium chloride solution heated to 40°, and allowing the filtered extract to cool. The proteid separated in isometric crystals. The filtrate on diluting gave a further precipitate, which was united with the first and recrystallised according to the method used by Grübler in his work on the squash-seed. A perfectly crystallised product was thus obtained, consisting of "octahedra, rhombodedecahedra and other forms of the regular system."

In a subsequent paper[2] Ritthausen published the results of his analyses of this proteid. Four preparations were made and analysed, only one of which, however, was crystallised. These were obtained: *d*, by diluting the sodium-chloride extract with water; *e*, by extracting *d* with 20-per cent. sodium chloride solution and preparing the insoluble portion for analysis; *f*, by crystallising *d* by Drechsel's method; *g*, by extracting the seeds with $\frac{1}{10}$-per cent. potash solution. The composition of these products was as follows:

	RITTHAUSEN.			
	d.	*e.*	*f.* Crystals.	*g.*
Carbon	50.94	51.33	50.98	51.19
Hydrogen	6.85	6.84	6.92	6.97
Nitrogen	18.62	18.80	18.73	18.06
Sulphur	0.8	0.82	0.82	0.92
Oxygen	22.74	22.21	22.55	22.86
	100.00	100.00	100.00	100.00

These analyses agreed with the results first obtained by Grübler for the proteid of the squash-seed, with the exception of carbon, of which Grübler found 53.30 per cent. Ritthausen[3] then procured some of Grübler's preparation and redetermined the carbon, finding as an average of four analyses 51.61 per cent. This result has since been confirmed by Grübler himself,[4] who now gives the percentage of carbon as 51.48 per cent.

It will be noticed that the carbon of Ritthausen's crystallised preparation is 0.5 per cent. lower than these figures and throws some doubt on the identity of these substances. In order to clear up this point, 100 grams of ground hemp-seeds—from which the oil had been removed by extracting with benzine, and the greater part of the hulls separated by passing through a fine sieve—were extracted with 10-per cent. sodium chloride solution and the filtered extract placed in a dialyser set in running water. After five days a large deposit was found in the dialyser, consisting almost wholly of octahedral crystals mixed with a few spheroids. This substance was filtered off, washed with water, alcohol and ether and dried over sulphuric acid. 7.8 grams were so obtained, which, when dried at 110°, had the following composition:

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[1] J. prakt. Chem. **23**, 481. [2] *Ibid.* **25**, 130. [3] *Ibid.* **25**, 137 [4] *Ibid.* **44**, 369.

HEMP-SEED GLOBULIN: *Crystals—Preparation* 4.

		Ash-free.
Carbon	51.00	51.26
Hydrogen	6.83	6.86
Nitrogen	18.59	18.68
Sulphur	0.94	0.94
Oxygen	..	22.26
Ash	0.50	..
		100.00

Ash.—0.4042 gram substance, dried at 110°, gave 0.0020 gram ash = 0.50 per cent.

Carbon and hydrogen.—0.2977 gram dried substance gave 0.5567 gram CO_2 = 51.00 per cent. C, and 0.1840 gram H_2O = 6.83 per cent. H.

Nitrogen.—0.3464 gram dried substance gave 53.96 cc. N at 6° (barometer 741.7 mm. at 22°) = 18.59 per cent.

Sulphur.—0.9930 gram dried substance gave 0.0670 gram $BaSO_4$ = 0.92 per cent. S.

Another preparation was made by extracting 200 grams of ground hemp-seeds, freed from oil, with two liters of 5-per cent. sodium chloride solution heated to 60°, and filtering while hot. On cooling gradually to 5° a large amount of substance separated, which consisted wholly of octahedral crystals. This substance was then filtered off and washed with water. After most of the salt had been washed out, the preparation began to dissolve, the washings being precipitated on falling into the filtrate containing sodium chloride. Dilute alcohol was then substituted for water and the washing continued, the alcohol being gradually increased in strength to absolute. After washing next with ether the preparation was dried over sulphuric acid, and weighed 12.25 grams. Dried at 110° it had the following composition:

HEMP-SEED GLOBULIN: *Crystals—Preparation* 5.

		Ash-free.
Carbon	51.24	51.28
Hydrogen	6.84	6.84
Nitrogen	18.83	18.84
Sulphur	0.87	0 87
Oxygen	..	22.17
Ash	0.07	..
		100.00

Ash.—0.7188 gram substance, dried at 110°, gave 0.0005 gram ash = 0.07 per cent.

Carbon and hydrogen.—0.4022 gram dried substance gave 0.7556 gram CO_2 = 51.24 per cent. C, and 0.2477 gram H_2O = 6.84 per cent. H.

Nitrogen.—0.3495 gram dried substance gave 54.16 cc. N at 6° (barometer 754.7 mm. at 23°) = 18.83 per cent.

Sulphur.—0.9355 gram dried substance gave 0.0597 gram $BaSO_4$ = 0.87 per cent. S.

A small amount of substance similarly prepared was found to contain, dried at 110°, 18.72 per cent N and 0.30 of ash, or, ash-free, 18.77 per cent. N. All these analyses are here brought together.

HEMP-SEED GLOBULIN.

	Ritthausen.				Osborne.	
	d.	*e.*	*f.* Crystals.	*g.*	4. Crystals.	5. Crystals.
Carbon	50.94	51.33	50.98	51.19	51.26	51.28
Hydrogen	6.85	6.84	6.92	6.97	6.86	6.84
Nitrogen	18.62	18.80	18.73	18.06	18.68	18.84
Sulphur	0.85	0.82	0.82	0.92	0.94	0.87
Oxygen	22.74	22.21	22.55	22.86	22.26	22.17
	100.00	100.00	100.00	100.00	100.00	100.00

The crystallised preparations, *f*, 4 and 5 are in close agreement in all respects, excepting the carbon of *f*, which is somewhat low. Ritthausen's analyses *e* and *g* agree with the writer's and it is therefore almost certain that these are very nearly correct. That Ritthausen's carbon was a little too low was probably due to the fact that these crystalline preparations absorb moisture with great rapidity. Preparations which had been dried at 110° and preserved in closely-corked bottles in a desiccator were found to have absorbed from 0.5 to 1.0 per cent. of moisture in consequence of the brief exposure to the air incurred in removing the portions required for nitrogen determinations. The figures obtained for nitrogen agree as closely as could be expected, with the exception of that for *g*, which is unquestionably too low.

As 5 was perfectly crystallised and undoubtedly pure, its analysis may safely be taken as closely representing the true composition of this proteid. The reactions of this body were found to be as follows:

In pure water 4 was wholly insoluble, even on heating to 50°; on the other hand, 5 yielded a turbid solution with distilled water, becoming very nearly clear on warming to 50°. 4 was prepared by dialysis; 5 by cooling a warm sodium chloride solution. A similar difference for preparations made in these two ways was noticed in the globulin of the oat-kernel,[1] and also in that of the castor-bean, next to be described. The solution in water is precipitated on adding a little sodium chloride; the precipitate so produced being soluble on a further addition of this salt. 4 is wholly insoluble in glycerin, either concentrated or dilute, while 5 dissolves to a perfectly clear liquid, which is not precipitated by dilution, but is precipitated by adding a little salt, the substance redissolving on adding more salt. Both preparations dissolve in solutions of sodium chloride at 20°. The solubility increases with the temperature up to 60° or over. Near 0° very little, if any, dissolves in 10-per cent. sodium chloride solution. Saturation of the sodium chloride solution of this globulin with salt produces a trifling precipitate; saturation with ammonium sulphate gives a complete precipitation, as does also saturation with magnesium sulphate. It is very soluble in distilled water containing a minute amount of acid. Preparation 5 dissolves instantly and completely in $\frac{5}{10000}$-per cent. hydrochloric acid, provided enough is taken to combine with all the substance present. 4, on the other hand, requires a somewhat stronger acid, but is readily soluble in $\frac{2}{100}$-per cent. hydrochloric acid. Very dilute solutions of sodium carbonate (about $\frac{1}{10}$ per cent.) dissolve both preparations readily and completely, as do also solutions of caustic alkalies. Dissolved in 10-per cent. sodium chloride solution, a turbidity occurs on heating to 75°, and flocks form at 86°. If the solution is then filtered and again heated, turbidity results a second time at 88°, flocks forming at 95°. The amount of substance separated at 86° is hardly more than a trace and undoubtedly indicates the presence of an extremely small amount of some other proteid, for if the sodium chloride solution is saturated with salt and the trifling precipitate produced is filtered off and the filtrate diluted until it contains 10-per cent. of sodium chloride, it first becomes turbid when heated to 87°, and no flocks appear until heated to 94°. If the solution is then raised to 98°, kept at that temperature for some time, filtered from the coagulum and boiled, no more precipitate is produced. If acid be added a very heavy precipitate falls, showing either that the globulin is only partly precipitated at 100°, or that it undergoes a change, a portion being converted into a proteid unaffected by boiling. This substance gives all the reactions common to proteids.

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[1] This Journal **13**, 408.

The crystals in which this proteid usually separates are simple octahedrons, although modifications of this form are frequently to be seen. Occasionally hexagonal plates may be found among the octahedrons. In two cases where this body was crystallised in small quantity, the entire crop of crystals consisted of very thin hexagonal plates.

The facility with which crystals of this proteid can be obtained is very remarkable, it separating in this form whenever precipitated by dialysing or by cooling its solutions. The other seeds from which crystallised proteids have thus far been obtained yield well-crystallised products only with considerable difficulty, as the proteid usually separates in the spheroidal form.

CRYSTALLINE PROTEID OF THE CASTOR-BEAN.

Ritthausen[1] first obtained the globulin of the castor-bean in a well-crystallised condition by following Grübler's method. Subsequently[2] he gave the results of his analyses of this substance (*h*), which were as follows:

As the mean of several analyses of two preparations, previously described,[3] obtained by extracting the seeds with sodium chloride solution and precipitating the extracts by diluting and passing through them carbonic acid gas, Ritthausen also gave the figures *i* and *j*.

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[1] J. prakt. Chem. **23**, 481.

[2] *Ibid.* **25**, 130.

[3] Pflüger's Archiv **19**, 15.

CASTOR-BEAN GLOBULIN.—*Ritthausen.*

	h. Crystals.	*i.*	*j.*
Carbon	50.88	52.05	51.31
Hydrogen	6.98	6.83	6.90
Nitrogen	18.58	18.57	18.43
Sulphur	0.77	0.96	0.97
Oxygen	22.79	21.59	22.39
	100.00	100.00	100.00

As these analyses leave the composition of this proteid in doubt, and since many of the reactions now considered important were not given by Ritthausen, this substance has been reinvestigated by the writer. The material for the preparation of this proteid was obtained by freeing the castor-beans from their shells, bruising the meats in a mortar, extracting the oil with ether, and pulverising the residue. 60 grams of this meal were extracted with 10-per cent. sodium chloride brine and the filtered extract placed in a dialyser. After removal of the chlorides, the separated proteid was filtered off, washed with water, alcohol and ether, and dried over sulphuric acid. 4.25 grams of material were so obtained, consisting of spheroids and crystals mixed with intermediate forms. After drying at 110°, this preparation was analysed with the following result:

CASTOR-BEAN GLOBULIN: *Crystals and Spheroids.—Preparation* 6.

		Ash-free.
Carbon	51.57	51.62
Hydrogen	6.92	6.92
Nitrogen	18.79	18.81
Sulphur	0.76	0.76
Oxygen	..	21.89
Ash	0.10	..
		100.00

Ash.—0.5615 gram substance, dried at 110°, gave 0.0006 gram ash = 0.10 per cent.

Carbon and hydrogen.—0.3069 gram dried substance gave 0.5803 gram CO_2 = 51.57 per cent. C, and 0.1914 gram H_2O = 6.92 per cent. H.

Nitrogen.—0.2855 gram dried substance gave 43.64 cc. N at 6° (barometer 763.3 mm. at 23°) = 18.79 per cent.

Sulphur.—0.9173 gram dried substance gave 0.0503 gram $BaSO_4$ = 0.76 per cent. S.

Another extraction was made by treating 75 grams of the fine oil-free meal with 1000 cc. of a 5-per cent. sodium chloride solution heated to 60°, filtering perfectly clear and allowing the extract to cool to 5°. A considerable amount of substance separated, which was filtered off and washed with water, in which it was found to dissolve when the salt was nearly all removed. The entire precipitate was then dissolved in 10-per cent. sodium chloride brine and the resulting clear solution saturated with salt. This produced a considerable precipitate, which was filtered off and washed with a saturated salt solution. The filtrate and washings were then put in a dialyser.

The portion precipitated by saturation with sodium chloride was dissolved in a dilute solution of this salt and likewise submitted to dialysis. After the contents of the dialysers had become free from chlorides the precipitates were filtered off, washed with alcohol and ether, and dried over sulphuric acid. The preparation obtained from the *precipitate* produced by saturation with sodium chloride weighed 3.3 grams and consisted of imperfectly formed crystals and spheroids; while that obtained from the saturated salt *solution* weighed 2.5 grams and was likewise partly crystalline. These two preparations were analysed, the composition of the former being shown by the analysis of preparation 7, the latter by that of 8.

CASTOR-BEAN GLOBULIN: *Crystals and spheroids insoluble in saturated sodium chloride solution*—7.

	Ash-free.		Average.
	I.	II.	
Carbon	51.40	51.29	51.35
Hydrogen	6.81	6.86	6.84
Nitrogen	18.88	..	18.88
Sulphur	0.79	..	0.79
Oxygen	..	..	22.14
Ash	0.00	..	..
			100.00

Ash.—0.6773 gram substance, dried at 110°, gave no weighable ash.

Carbon and hydrogen, I.—0.3614 gram dried substance gave 0.6811 gram CO_2 = 51.40 per cent. C, and 0.2215 gram H_2O = 6.81 per cent. H.

II.—0.3544 gram dried substance gave 0.6664 gram CO_2 = 51.29 per cent. C, and 0.2187 gram H_2O = 6.86 per cent. H.

Nitrogen.—0.3481 gram dried substance gave 53.55 cc. N at 6° (barometer 762.3 mm. at 23.5°) = 18.88 per cent.

Sulphur.—0.7960 gram dried substance gave 0.0460 gram $BaSO_4 = 0.79$ per cent. S.

CASTOR-BEAN GLOBULIN: *Crystals and spheroids soluble in saturated sodium chloride solution*—8.

	I.	II.	Average.	Ash-free.
Carbon	51.14	50.99	51.07	51.19
Hydrogen	6.82	6.81	6.82	6.84
Nitrogen	18.88	..	18.88	18.92
Sulphur Oxygen	..	..	..	23.05
Ash	0.24	..	0.24	..
				100.00

Ash.—0.4480 gram substance, dried at 110°, gave 0.0011 gram ash = 0.24 per cent.

Carbon and hydrogen, I.—0.3483 gram dried substance gave 0.6531 gram $CO_2 = 51.14$ per cent. C, and 0.2137 gram $H_2O = 6.82$ per cent. H.

II.—0.3485 gram dried substance gave 0.6516 gram $CO_2 = 50.99$ per cent. C, and 0.2136 gram $H_2O = 6.81$ per cent. H.

Nitrogen.—0.2987 gram dried substance gave 46.05 cc. N at 6° barometer 760.2 mm. at 22°) = 18.88 per cent.

The filtrate from the precipitate, produced by cooling the 5-per cent. sodium chloride extract last described, was heated to 40° in a water-bath, and twice its volume of distilled water heated to 40° was added. A perfectly clear solution resulted, which when slowly cooled to 5° yielded a well-crystallised precipitate, the crystals being almost exclusively octahedrons with one angle truncated. This precipitate was filtered off, washed with water, alcohol and ether, and when dried over sulphuric acid weighed 3.5 grams. Dried at 110°, this preparation was found to have the following composition:

CASTOR-BEAN GLOBULIN: *Crystals—Preparation* 9.

	I.	II.	Average.	Ash-free.
Carbon	51.31	51.26	51.29	51.31
Hydrogen	6.94	7.00	6.97	6.97
Nitrogen	18.75	..	18.75	18.75
Sulphur	0.70	0.82	0.76	0.76
Oxygen	..	..	..	22.21
Ash	0.03	..	0.03	..
				100.00

Ash.—0.6315 gram substance, dried at 110°, gave 0.0002 gram ash = 0.03 per cent.

Carbon and hydrogen, I.—0.3157 gram dried substance gave 0.5939 gram CO_2 = 51.31 per cent. C, and 0.1969 gram H_2O = 6.94 per cent. II.

II.—0.3976 gram dried substance gave 0.7473 gram CO_2 = 51.26 per cent. C, and 0.2516 gram H_2O = 7.00 per cent. H.

Nitrogen.—0.3074 gram dried substance gave 48.1 cc. N at 6° (barometer 744.0 mm. at 21°) = 18.75 per cent.

Sulphur, I.—0.5468 gram dried substance gave 0.0273 gram $BaSO_4$ = 0.70 per cent. S.

II.—0.4588 gram dried substance gave 0.0275 gram $BaSO_4$ = 0.82 per cent. S.

The following table shows the results of the analyses of Ritthausen and the writer:

CASTOR-BEAN GLOBULIN.

	Ritthausen.			Osborne.			
	h	*i*	*j*	6	7	8	9
	Crystals.			Crystals and Spheroids.			Crystals.
Carbon	50.88	52.05	51.31	51.62	51.35	51.19	51.31
Hydrogen	6.98	6.83	6.90	6.92	6.84	6.84	6.97
Nitrogen	18.58	18.57	18.43	18.81	18.88	18.92	18.75
Sulphur	0.77	0.96	0.97	0.76	0.79	23.05	0.76
Oxygen	22.79	21.59	22.39	21.89	22.14		22.21
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

This table shows plainly that Ritthausen's figure for carbon in the analysis of his crystallised preparation is too low, probably because the sample had taken up a little moisture from the air, as explained before in discussing the analyses of the hemp-seed proteids. Apart from this, Ritthausen's analysis of his crystallised preparation agrees well with those of the writer.

The analysis of the perfectly crystallised preparation 9 may be taken as closely representing the true composition of this proteid.

In pure water this substance behaved like that obtained from the hemp-seed—that is, preparations separated by dialysis were insoluble in water, either at 20° or 50°; those separated by cooling warm saline solutions were soluble to opalescent solutions at 20°, becoming clear on warming. Solutions in water are precipitated by a small quantity of sodium chloride, the precipitate dissolving on adding a larger quantity of the salt. Preparations 7 and 8, which dissolved in water when first separated from the warm solution, after being redissolved and then precipitated by dialysis, were wholly insoluble in water.

Toward glycerin this proteid behaves in the same way as the hemp-seed globulin. Some of the preparations made dissolved completely, others partly, in a 10-per cent. sodium chloride solution, leaving a considerable insoluble residue (Weyl's "albuminate"), which, however, dissolved almost wholly on warming to 50°, a part separating in spheroids when the solution was cooled.

Saturation of the salt-solution with ammonium sulphate completely precipitates this proteid. Saturation with sodium chloride precipitates a large part of the globulin contained in the extract of the seed, the part precipitated and that remaining in solution being alike in most of their reactions and composition.

It is probable that the precipitate produced by saturation with sodium chloride solution is caused by a small amount of some other substance extracted from the seed, for the crystalline preparation 9, which was obtained from the extract after previous precipitation of a part of the globulin contained in it, gave on saturation with this salt only a trifling precipitate. A part of the precipitate is also unquestionably due to a small amount of another globulin coagulating at from 75° to 86°, for where this precipitate is dissolved in 10-per cent. sodium chloride brine and heated to this temperature, a much larger coagulum is produced than when the substance obtained from the salt-saturated solution is similarly treated. The perfectly crystalline preparation 9, which yields but a very small amount of precipitate on saturating its salt-solution with sodium chloride, likewise gives but a trace of coagulum when heated to 89°. The crystalline globulin is therefore not precipitated by saturation with sodium chloride.

Dissolved in 10 per cent. sodium chloride solution, the crystalline preparation 9 became turbid when heated to 87°, and at 89° a very minute amount of flocks separated. At 95° a large coagulum developed and, on heating the solution for some time at 98°, after filtering off the coagulum, the filtrate gave only a turbidity when boiled, but on adding acid a very large precipitate fell, showing that the globulin is but partly precipitated by heat.

The other preparations behaved, on heating their salt-solutions, in exactly the same way, except that the coagulum separating at the lower temperature was somewhat greater in amount.

This proteid can be crystallised only with difficulty, being in this respect very different from the globulin of the hemp-seed. It is not improbable that this is due to other constituents of the seed which interfere to a greater or less extent with the formation of the crystals.

THE CRYSTALLINE PROTEID OF THE FLAX-SEED.

In a former paper[1] the writer has described a crystallised globulin obtained from flax-seed, the appearance of the crystals being shown by the accompanying plate. As the mean of a large number of accordant analyses its composition was given as follows:

CRYSTALLISED FLAX-SEED GLOBULIN.

Carbon	51.48
Hydrogen	6.94
Nitrogen	18.60
Sulphur	0.81
Oxygen	22.17
	100.00

In pure distilled water at 20° this proteid, whether separated from solution by cooling or by dialysis, is wholly insoluble, while in water at 40° it is very slightly soluble. In 10 per cent. sodium chloride solution it is mostly soluble, a part (Weyl's "albuminate") generally remaining undissolved, which, however, dissolves readily on warming the solution and partly separates, on cooling, in very finely developed crystals. In glycerin diluted with water the substance separated by dialysis is wholly insoluble, either at 20° or 40°; while the substance separated from a warm sodium chloride solution is largely soluble at 20°.

Saturation with ammonium sulphate and also with magnesium sulphate completely precipitates this proteid from its solutions. Saturation with sodium chloride gives a small precipitate which consists partly of other globulins, for the filtrate from this precipitate, when diluted so as to contain 10 per cent. of sodium chloride, yields but a trace of coagulum on heating to boiling, while the precipitate dissolved in 10-per cent. sodium chloride coagulated at the various temperatures observed in the solution before saturation.

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[1] This Journal **14**, 629.

In very dilute acids—as $\frac{1}{50}$-per cent. hydrochloric acid or $\frac{1}{10}$-per cent. citric acid—the proteid readily and completely dissolves to solutions which are precipitated by adding a little sodium chloride. In $\frac{1}{10}$-per cent. sodium carbonate solution or $\frac{1}{100}$-per cent. potash solution the substance dissolves at once.

On heating a 10-per cent. sodium chloride solution of this globulin small amounts of substance separate at different temperatures, according to the method employed in the preparation of the proteid. The substances coagulating below 90° are undoubtedly traces of other globulins, as already stated. These globulins are also separated from the crystalline globulin if the latter is precipitated from solution by cooling, and after washing with water, alcohol and ether and drying over sulphuric acid, is then dissolved in 10-per cent. sodium chloride brine. Thus separated from these coagulable proteids, boiling produces but a trace of a coagulum, while in the case of the globulin obtained by dialysis the coagulum produced by boiling is a little greater. In any case the coagulation produced by boiling is only partial, for a very large precipitate is always obtained on adding acid to these solutions, even after boiling them for some time. The crystals of this proteid were always obtained as octahedrons.

THE CRYSTALLISED PROTEID OF THE OAT-KERNEL.

In this Journal[1] and also in the Report of the Connecticut Agricultural Experiment Station for 1891, the writer described a globulin from the oat-kernel which was obtained in a perfectly crystallised condition. The form of these crystals is shown in the plate.

As an average of three closely agreeing analyses of different preparations, its composition was found to be as follows:

CRYSTALLISED OAT-GLOBULIN.

Carbon	52.18
Hydrogen	7.05
Nitrogen	17.90
Sulphur	0.53
Oxygen	22.34
	100.00

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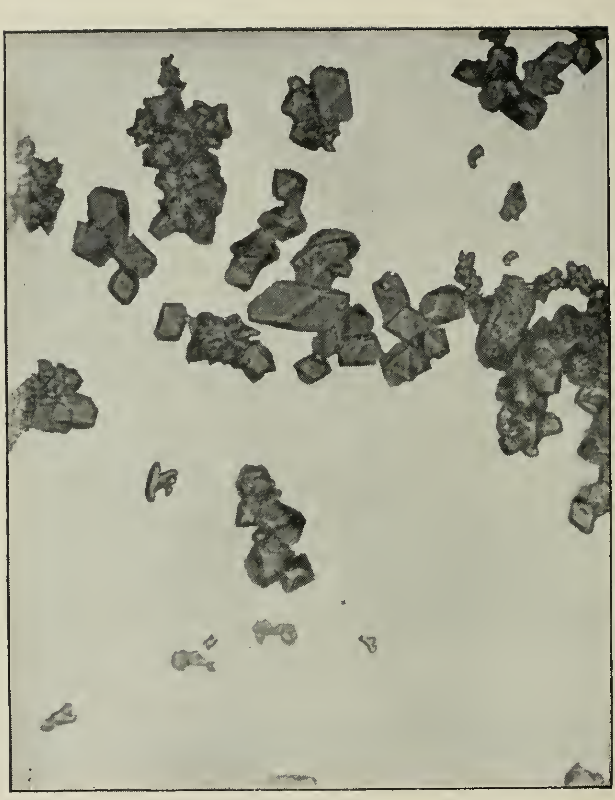
[1] This Journal **13**, 408; **14**, 212.



CRYSTALLISED GLOBULIN OF THE OAT KERNEL.

In distilled water at 20° this proteid in the crystallised condition is not soluble; in the spheroidal condition, separated from a warm sodium chloride solution, by boiling it yields an opalescent solution. On slowly warming, the crystals partly dissolve, while the spheroids quickly give a clear solution. Addition of a little sodium chloride precipitates these solutions, but the addition of a further quantity of this salt redissolves the precipitate. In 10-per cent. sodium chloride the crystals dissolve at 20°, with the exception of a slight residue which is nearly completely dissolved by warming. This solution is not precipitated by boiling. Dilution precipitates the proteid.

In diluted glycerin most of the substance dissolves. Saturation with ammonium sulphate and with magnesium sulphate completely precipitates solutions of this proteid in sodium chloride brine. Saturation with sodium chloride likewise precipitates such solutions. In very dilute acids, $\frac{2}{100}$-per cent. hydrochloric acid or $\frac{1}{2}$-per cent. citric acid, it is readily soluble to a perfectly clear solution. In $\frac{1}{2}$-per cent. sodium carbonate solution the crystals are soluble with the exception of a slight residue; the spheroids, on the other hand, with $\frac{1}{10}$-per cent. sodium carbonate give at once a perfectly clear solution. In $\frac{1}{100}$-per cent. potash solution both spheroids and crystals are at once dissolved to a perfectly clear solution.

THE CRYSTALLISED PROTEID OF THE SQUASH-SEED.

This proteid was first prepared and analysed by Barbieri,[1] whose preparations, however, were not crystalline; soon after Grübler,[2] employing a method suggested by Drechsel, succeeded in obtaining perfectly crystallised preparations of this substance and published the results of his observations and analyses. The percentage of carbon found by Grübler was shown by Ritthausen[3] to be too high, owing to the use of an imperfect method for the determination of this element.

Later Chittenden and Hartwell[4] prepared this proteid in the crystallised form for use in digestion experiments, and published analyses confirming those of Ritthausen. Grübler[5] has lately made a new analysis of this body nearly according with the results of Ritthausen and with those of Chittenden and Hartwell.

[1] J. prakt. Chem. [2] **18**, 102.

[2] *Ibid.* [2] **23**, 97.

[3] *Ibid.* [2] **23**, 481.

[4] J. Physiol. **11**, 435.

[5] J. prakt. Chem. [2] **44**, 369.

As, however, the analyses of these investigators do not harmonise in all respects, the writer has examined this proteid with the hope of fixing its composition more nearly.

A quantity of squash-seeds, freed from hulls and finely chopped, were extracted with ether. The coarse powder was then thrown on a straining cloth and the finest portions washed through together with the ether. The coarse meal remaining in the cloth was then ground in a mortar and again washed on the cloth with ether. After freeing from most of the oil and drying in the air, 50 grams of coarse meal were obtained from 200 grams of freshly-shelled meats. The fine meal passing through the cloth was collected on a filter and washed with ether until fat-free, and, after drying in the air, weighed 70 grams, all of which passed through a sieve with holes $\frac{1}{50}$-inch in diameter.

Fifty grams of the coarse meal were then treated with 800 cc. of 2-per cent. sodium chloride solution heated to 60°, and at once thrown on to a filter. The clear extract was allowed to cool in a beaker left over night in a room having a temperature of about 10°. In the morning a large deposit had separated, entirely composed of perfectly formed octahedrons. This was filtered off, washed once with water and then thoroughly with 50-per cent. alcohol, then with absolute alcohol and finally with ether, and dried over sulphuric acid. A snow-white preparation, weighing 9 grams, was thus obtained, which was dried at 110° and analysed with the following results:

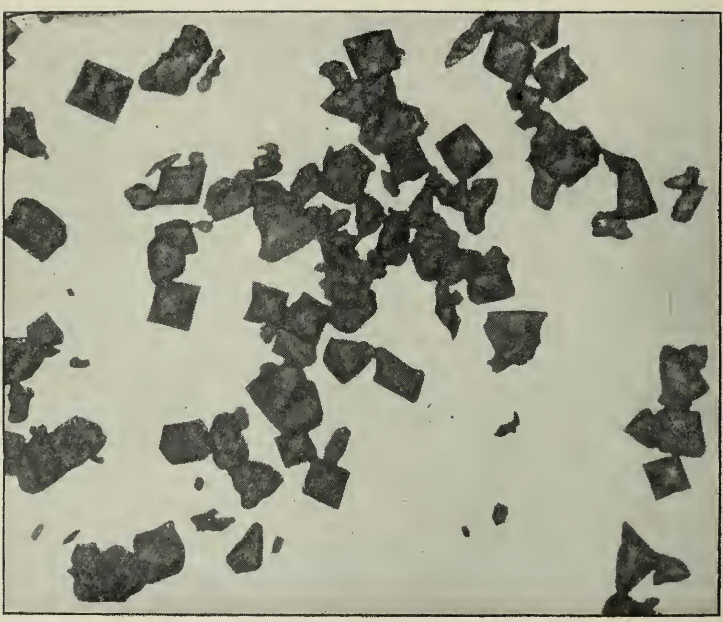
SQUASH-SEED PROTEID: *Crystallised—Preparation* **10.**

	I.	II.	III.	Average.	Ash-free.
Carbon	51.49	51.64	51.74	51.62	51.66
Hydrogen	6.88	6.92	6.84	6.88	6.89
Nitrogen	18.50	18.49	...	18.50	18.51
Sulphur	0.88	0.87	...	0.88	0.88
Oxygen	...	...	...	...	22.06
Ash	0.08	...	...	...	...
					100.00

Ash.—0.4789 gram substance, dried at 110°, gave 0.0004 gram ash = 0.08 per cent.

Carbon and hydrogen, I—0.3868 gram dried substance gave 0.7303 gram CO_2 = 51.49 per cent. C, and 0.2394 gram H_2O = 6.88 per cent. H.

II.—0.3986 gram dried substance gave 0.7548 gram CO_2 = 51.64 per cent. C, and 0.2484 gram H_2O = 6.92 per cent. H.



CRYSTALLISED GLOBULIN OF FLAX-SEED.

III.—0.3116 gram dried substance gave 0.5917 gram $CO_2 = 51.74$ per cent. C, and 0.1919 gram $H_2O = 6.84$ per cent. H.

Nitrogen, I.—0.2577 gram dried substance gave 39.21 cc. N at 10° (barometer 765.4 mm. at 21°) = 18.50 per cent.

II.—0.3881 gram dried substance gave 59.32 cc. N at 11° (barometer 764.7 mm. at 24°) = 18.49 per cent.

Sulphur, I.—0.7086 gram dried substance gave 0.0457 gram $BaSO_4 = 0.88$ per cent. S.

II.—0.7804 gram dried substance gave 0.0493 gram $BaSO_4 = 0.87$ per cent. S.

Another preparation was made by extracting 50 grams of the fine meal with 10-per cent. sodium chloride solution at 20°, filtering from the insoluble residue and dialysing the clear extract. As the chloride was removed the proteid precipitated in the form of irregular granules together with some spheroids and crystals. After dialysing three days the large deposit was filtered off, washed with water, alcohol and ether, and dried over sulphuric acid. This preparation weighed 21.27 grams, and when dried at 110° was analysed with the following result:

SQUASH-SEED PROTEID: *Spheroids—Preparation* II.

	I.	II.	Average.	Ash-free.
Carbon	51.31	51.23	51.27	51.42
Hydrogen	6.82	6.80	6.81	6.83
Nitrogen	18.50	18.68	18.59	18.64
Sulphur	0.90	0.89	0.90	0.90
Oxygen	...	...	...	22.21
Ash	0.29	...	...	...
				100.00

Ash.—1.1487 grams substance, dried at 110°, gave 0.0033 gram ash = 0.29 per cent.

Carbon and hydrogen, I.—0.3835 gram dried substance gave 0.7215 gram $CO_2 = 51.31$ per cent. C, and 0.2356 gram $H_2O = 6.82$ per cent. H.

II.—0.3743 gram dried substance gave 0.7032 gram $CO_2 = 51.23$ per cent. C, and 0.2289 gram $H_2O = 6.80$ per cent. H.

Nitrogen, I.—0.3313 gram dried substance gave 50.64 cc. N at 11° (barometer 765 3 mm. at 23°) = 18.50 per cent.

II.—0.3761 gram dried substance gave 58.13 cc. N at 11° (barometer 764.0 mm. at 24°) = 18.68 per cent.

Sulphur, I.—0.6426 gram dried substance gave 0.0424 gram $BaSO_4 = 0.90$ per cent. S.

II.—0.8344 gram dried substance gave 0.0545 gram $BaSO_4 = 0.89$ per cent. S.

The following table gives the results obtained by all the chemists who have analysed this substance:

		Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.
Barbieri, amorphous		51.88	7.51	18.08	0.60	21.93
Grübler's 1st analyses,	crystals	53.21	7.22	19.22	1.07	19.10
Ritthausen	"	51.61	7.00	...	...	...
Chittenden and Hartwell,	"	51.60	6.97	18.80	1.01	21.62
" "	spheroids	52.03	6.93	19.08	1.04	20.92
" "	amorphous	51.81	6.94	18.71	1.01	21.53
Grübler's 2d analyses,	crystals	51.48	6.76	18.14	0.96	21.53
10 Osborne	"	51.66	6.89	18.51	0.88	22.06
11 "	spheroids	51.42	6.83	18.64	0.90	22.21

If we omit Grübler's first analysis, which, as already stated, is incorrect, the average of the remaining eight is

Carbon	51.69
Hydrogen	6.97
Nitrogen	18.57
Sulphur	0.91
Oxygen	21.86
	100.00

The reactions of the preparations made by the writer were as follows:

In distilled water either at 20° or warmed to 60° the preparations, whether separated from solution in sodium chloride brine by dialysis or by cooling, were wholly insoluble. In glycerin, either strong or diluted, they were likewise insoluble, even when warmed to 60°. In 10-per cent. sodium chloride solution they both dissolved with the exception of a mere trace, and the resulting solutions were not precipitated by saturating with sodium chloride, but were completely precipitated by saturation with ammonium sulphate and also with magnesium sulphate. In $\frac{2}{100}$-per cent. hydrochloric acid and $\frac{1}{10}$-per cent. citric acid both yielded perfectly clear solutions when sufficient acid was employed to form an acid compound with the proteid. In $\frac{1}{10}$-per cent. sodium carbonate and $\frac{1}{100}$-per cent. potash solutions the preparations dissolved readily and completely; these solutions were not precipitated by sodium chloride. When dissolved in 10-per cent. sodium chloride solution and heated to coagulation the two preparations behaved somewhat differently, as is best shown by the following table: A being the preparation obtained by cooling the warm 2-per cent. sodium-chloride extract; B, that precipitated by dialysis.

HEAT-COAGULATION OF SQUASH-SEED GLOBULIN.

	A.	B.	
Turbidity at	..	73°	Small precipitate.
Flocks at	..	84	
After filtering at	87°	..	
Turbidity	87	87 [?]	
Flocks	95	95	
After filtering and boiling	no coagulum.	no coagulum.	

On adding a drop of acetic acid both yielded a large precipitate. These figures indicate that B contains a small amount of some other globulin which coagulates between 73° and 84°.

CONCLUSIONS.

I. The data presented in this paper indicate that the crystallised globulins of the Brazil-nut and of the oat-kernel are distinct substances. To facilitate comparison, analyses of these two globulins are here stated as follows:

	BRAZIL-NUT.	OAT-KERNEL.
	1.	Average.
Carbon	52.18	52.18
Hydrogen	6.92	7.05
Nitrogen	18.30	17.99
Sulphur	1.06	0.53
Oxygen	21.54	22.34
	100.00	100.00

If the differences in nitrogen- and sulphur-content are not perhaps sufficient to distinguish these two proteids, their reactions prove them to be distinct, for when prepared in the same manner they are unlike in many respects.

In distilled water heated to 60° the globulin of the Brazil-nut is wholly insoluble, while that of the oat-kernel dissolves completely. Saturation of a 10-per cent. sodium chloride solution of these substances with salt almost completely precipitates the proteid of the oat-kernel, that of the Brazil-nut being unaffected. Saturation of similar solutions with magnesium sulphate precipitates but little of the Brazil-nut, but all of the oat-globulin. When solutions of these bodies in 10-per cent. sodium chloride brine are heated, the Brazil-nut globulin begins to separate at 70°, a flocculent coagulum forming at 84°, which increases on raising the temperature to boiling, the proteid being largely, but not wholly, precipitated. The globulin of the oat-kernel, on the other hand, is not coagulated at all by boiling.

II. The crystalline globulins of the hemp-seed, castor-bean, squash-seed and flax-seed are almost identical in composition, as may be seen by comparing the analyses:

	Hemp-seed. 5.	Castor-bean. 9.	Squash-seed. 10.	Flax-seed. Average.
Carbon	51.28	51.31	51.66	51.48
Hydrogen	6.84	6.97	6.89	6.94
Nitrogen	18.84	18.75	18.51	18.60
Sulphur	0.87	0.76	0.88	0.81
Oxygen	22.17	22.21	22.06	22.17
	100.00	100.00	100.00	100.00

The carbon content of the hemp- and castor-globulins is less than that of the squash- and flax-globulins by about 0.25 per cent., a difference too slight to have importance, if it were not constant for almost all the preparations analysed. The deportment of these globulins toward reagents is also very similar, but in this respect the hemp- and castor-globulins show slight differences from those of the squash- and flax-seed; the two former are, however, almost exactly alike, and the two latter likewise closely agree together. The following table plainly exhibits these relations:

HEAT-COAGULATIONS.

	Hemp.	Castor.	Squash.	Flax.
Turbidity,	75°	87°	..	67°
Flocks,	86	89	..	80
Filtered,				
Turbidity,	88	87	87	90
Flocks,	95	95	95	96
Filtered,				
Boiling,	no coagulum.	ditto.	ditto.	ditto.
Filtered and acetic acid added,	heavy pp.	ditto.	ditto.	ditto.

SOLUBILITY.[1]

	Hemp.[2]		Castor.		Squash.	Flax.	
	A.	B.	A.	B.	A. B.	A.	B.
H_2O at 20°,	P.	I.	P.	I.	I.	I.	I.
H_2O at 40°,	S.	I.	S.	I.	I.	P.	I.
Glycerine at 20°,	S.	I.	S.	I.	I.	P.	I.
Glycerine at 50°,	S.	I.	S.	I.	I.	P.	I.
10-per cent. NaCl sol. diluted,	Pp.	Pp.	Pp.	Pp.	Pp.	Pp.	Pp.
Saturated with NaCl,	T. pp.	T. pp.	T. pp.	T. pp.	No Pp.	V.	V.
Saturated with $MgSO_4$,	C. pp.	C. pp.	C. pp.	C. pp.	C. pp.	C. pp.	C. pp.

---

[1] P. = Partly soluble; I. = Insoluble; S. = Soluble; Pp. = Precipitate; T. pp. = Trace of precipitate; C. pp. = Completely precipitated; V. = Very little precipitate.

[2] A indicates preparations obtained by cooling warm salt solutions; B, those obtained by dialysis.

As already stated, the proteids coagulating at the lower temperature are traces of other globulins imperfectly separated from the crystalline globulin. The coagulum separating at the higher temperature is undoubtedly a part of the crystalline globulin which is broken up when heated to this temperature. It is seen that the temperature at which this coagulum separates is the same for all four substances.

In solubility these four proteids are very nearly alike, the most noticeable difference being that the globulins of the hemp-seed and castor-bean, when separated from a warm sodium-chloride solution, are soluble in water and diluted glycerin, while the other preparations, both of this substance and the globulins of other seeds, are insoluble under the same conditions.

Of the flax-seed globulin separated from a warm salt solution, a little dissolves in water at 40°.

The small precipitate obtained by saturating a sodium-chloride solution of the globulins with salt undoubtedly consists mostly of traces of other globulins.

It is at present impossible to assert that these four globulins are the same, but since differences exist between different preparations of globulin from the same seed as great as those found among the globulins of these different seeds, the writer is disposed to consider these four globulins as identical.

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INDEX VOL. XIV.

ABSORPTION-SPECTRA of thin metallic films and of incandescent vapors of the metals . . . 185
Acet-acetic ether and derivatives, new method of converting into pyrazolones . . . 516
Acet-acetic ether, constitution of the sodium compound . . . 481
Acet-acetic ether hydrazide, condensation products of . . . 576
Acetic esters substituted, saponification of . . . 366
Acet-methyl malonic ether, preparation and properties . . . 509
Acetoacetic ether, action of acetyl chloride on the phenyl hydrazide . . . 420
Acetoacetic ether, action of hydrobromic acid on . . . 421
“ “ “ “ phenyl hydrazine hydrochloride on . . . 417
“ “ some reactions with . . . 407
Acetylene, composition of the explosive copper and silver compounds of . . . 285
Acetyl chloride, action on sodium malonic ether . . . 495
“ “ “ “ the phenyl hydrazide of aceto-acetic ether . . . 420
Acetyl salicylic ether . . . 417
Agave Americana, sugar of, researches on . . . 548
Albuminoids or proteids of the oat kernel . . . 212
α-Aldehydo-β-naphthol . . . 298
Aluminium chloride, catalytic action on silicic ethers . . . 438
Amidoxyoxindol, chloride of . . . 362
Amidoparabromchlorbenzene . . . 561
Ammonium bromide and stannous bromide, compounds of . . . 96
Ammonium chloride, vapor density . . . 79
“ “ and stannous chloride, compounds of . . . 93
Ammonium chloro-manganite . . . 134
“ “ “ crystallography . . . 135
Anilidotrinitrophenylmalonic ester . . . 354
“ “ “ “ nitrite of . . . 341
Anilidotrinitrophenyltartronic ester . . . 347
Anilidotrinitrotoluol, sodium salt . . . 344
Antimony, double halides of . . . 152
Anthracene series, application of the Friedel-Crafts reaction to syntheses in the . . . 602

BAEYER, A. von. Constitution of benzene . . . 405
Barus, C. The volume lag and its bearing on molecular constitution . . . 191
Baskerville, C. See *Corse, M. B.*
Bentley, W. B. See *Jackson, C. L.*
Benzene, constitution of . . . 405
Benzo- and toluquinone, addition products of . . . 553
Benzoquinone, action of hydrochloric acid on . . . 571
“ preparation . . . 555
Benzyl silicate . . . 547
Benzoyl salicylic ether . . . 414
Berkeley, W. N. Analyses of paranthite from Clay County, North Carolina . . . 628
Bismuth and rubidium, complex chloride . . . 174
“ double halides of . . . 164
Blackshear, C. C. Dioxybenzoyl benzene sulphonic acid and sulphon fluorescein . . . 455
Black soil (Tschernozem) analyses . . . 621

Bradley, W. P., and *Dains, F. B.* Action of acetylchloride on orthohydroxy-aldehydes 293
Brazil-nut, crystallised proteid of 664
" globulin, crystals 667
Bridge, J. L. On the ethers of quinone-oxime (nitroso-phenol) 276
Brigham, C. P. On some double halides of bismuth 164
Bromdinitrophenylmalonic ester, nitrite of 358
Bromtrinitrophenylmalonic ester, action of nitric acid on 331
" " " " " nitrite of 336
" " " tartronic ester 345
Bruyn, L. de. Free hydroxylamine 76

CADMIUM, metallic, crystals of 273
Cadmium, redetermination of atomic weight 261
Calamine, electric, from Wythe County, Va., analysis 621
Calcium bismuth chlorides 179
Calcium chloro-manganites 143
" " " crystallography 145, 147
" " antimonite 152
Carb-ethoxyl-methyl-acet-acetic ether, preparation and properties 509
Carbohydrates, pentose, digestibility of 9
" of the coffee berry 473
Carbon dioxide in the urine 14
Castor-bean, crystalline proteid of 675
Catalytic action of aluminium chloride on silicic ethers 438
Cauffman, M. See *Orndorff, W. R.*
Chalmot, G. J. L. de. Condensation products of furfurol with aromatic bases 310
"Chemical Analysis of Iron" (*A. A. Blair*), review 70
Chemical research, Wolcott Gibbs fund for 252
"Chemical Technology" (*R. von Wagner*), review of English translation 250
Chittenden, R. H., and *Osborne, T. B.* Proteids of the corn or maize kernel 20
Chlorcarbonic ether, action on sodium malonic ether 498
" " " " " ethyl-acet-acetic ether 506
Chlornitrophenol 563
Chlorquinhydrone 574
" and quinone 575
Citronellone, an unsaturated fatty aldehyde 203
Clark, T. H. The addition products of benzo- and toluquinone 553
Coffee berry, carbohydrates of 473
Color-standard for natural waters 300
Corn or maize kernel, proteids of 20
Corse, M. B., and *Baskerville, C.* Analyses of glauconite from Hanover Co., Va. 627
Copper and silver compounds of acetylene, explosive 285
Copper sulphites 232
" sulphate, action of sulphur dioxide on, in presence of copper 232
Cream of tartar, solubility in diluted alcohol 624
Crismer, L. Free hydroxylamine 78
Cupric hydroxide, action of sulphur dioxide on 233
Cupric sulphite, basic 235
Cuproplumbite from Butte City, Montana, analysis 620

DAINS, F. B. See *Bradley, W. P.*
De Bell, J. T. Analysis of cuproplumbite from Butte City, Montana 620
" " Analyses of statuary marble from Rutland, Vt. 626
Desmotropism 240
Diammonium bromo-stannite 96
" " crystallographic measurements 104
Diammonium chloro-stannite 93
" " crystallographic measurements 102

Diazo compounds obtained from some of the nitronaphthylamine decomposition with alcohol . . . 45
Dibenzylcarbinamine and its conduct towards nitrous acid . . . 225
Dibenzyl carbinol . . . 229
Dibrom-dichlor-salicylic aldehyde . . . 296
Dibromsalicylic ether . . . 412
"Dictionary of Chemistry" (*T. E. Thorpe*), review . . . 246
Dinitrophenylenedimalonic ester, attempt to make . . . 362
Dioxybenzoyl benzene sulphonic acid . . . 455
Di-potassium bromo-stannite . . . 95
" " crystallographic measurements . . . 105
Di-potassium chloro-stannite . . . 91
" " crystallographic measurements . . . 101
" " bismuthite . . . 167
Disalicylic aldehyde . . . 293
Dissociation of salts into their ions by water of crystallisation . . . 604
Ditmar, W. Obituary note . . . 259
Double halides of antimony . . . 152
" " bismuth . . . 164
" " lead . . . 107
" " manganese . . . 127
" " tin . . . 89
" " researches on . . . 81
Dudley, W. L. Colors and absorption spectra of thin metallic films and of incandescent vapors of the metals, with some observations on electrical volatility . . . 185
Dunlap, F. L. See *Freer, P. C.*
Dunnington, F. P. Notes from the Chemical Laboratory of the University of Virginia 620
" " and *Whitlock, T. C.* Analyses of Tschernozem or black soil . . . 621
" " See *Kinney, W. J.*

ELECTRICAL VOLATILITY, observations on . . . 185
Electrolytic determination of metals as amalgams, letter regarding . . . 260
"Elementary Chemistry" (*G. F. Barker*), review . . . 249
Ethyl dibrom-acetate, saponification . . . 373
Ethyl dichlor-acetate, saponification . . . 371
Ethyl dichlorsilicate . . . 449
Ethylic-α-methylindol-β-carboxylate . . . 577
Ethylic(1)phenyl(5)ethoxypyrazol(3)carboxylate . . . 579
Ethylmonobrom acetate, saponification . . . 372
Ethyl monochlor acetate, saponification . . . 371
Ethyl monochlorsilicate . . . 450
Ethyl tribrom acetate, saponification . . . 374
Ethyl trichlor-acetate, saponification . . . 372
Ethyl trichlorsilicate . . . 448
Eupatorin: the active principle of *eupatorium perfoliatum* . . . 224
Ewell, E. E. The carbohydrates of the coffee berry . . . 473

FERRO-PENTACARBOXYL . . . 80
Fischer, E. The configuration of grape sugar and its isomers . . . 398
Flax-seed, proteids of . . . 629, 681
Formic acid, preparation . . . 259
Freer, P. C. Some reactions with aceto-acetic ether and with salicylic ether . . . 407
Freer, P. C., and *Dunlap, F. L.* On the saponification of the substituted acetic ethers . . . 366
Furfurol, condensation products with aromatic bases . . . 310
Friedel-Crafts reaction, application to syntheses in the anthracine series . . . 602
Fund for chemical research, the Wolcott Gibbs . . . 252

GAS ABSORPTIONS, an improved pipette for 231
Gibbs (Wolcott) fund for chemical research 253
" " Letter from to the editor 260
Gill, A. H. An improved pipette for gas absorptions 231
Glauconite from Hanover County, Va., analyses 627
Gomberg, M. Trimethylzanthine and some of its derivatives 611
Grape sugar and its isomers, configuration 399

HALIDES, double, of antimony 152
" " bismuth 164
" " lead 107
" " manganese 127
" " tin 89
" " researches on, 81
"Handbuch der Photographie" (*H. W. Vogel*), review 250
Hazen, A. A new color-standard for natural waters 300
Hemp-seed, crystallised proteid of 671
Herty, C. H. On the double halides of lead 107
Hillebrand, W. F., and *Melville, W. H.* Isomorphism and composition of thorium and uranous sulphates 1
Hofmann, A. W. von. Obituary note 329
"Hülfsbuch zur Ausführung chemischer Arbeiten" (*H. Schwanert*), review 247
Hunt, T. Sterry. Obituary note 258
Hydrazoic acid, preparation 78, 479
Hydroxy-aldehydes, ortho, action of acetyl chloride on 293
Hydroxylamine, free 76

"INDUSTRIAL Organic Chemistry" (*S. P. Sadtler*), review 72
"Inorganic Chemistry" (*W. Ramsay*), review 73
Iodomercurates of organic bases 608
Iodosobenzoic acid 478
Iridium, electrolytic separation from palladium and platinum 435
Iron-carbon-oxide 80

JACKSON, C. L., and *Bentley, W. B.* On the products obtained by the action of nitric acid upon bromtrinitrophenylmalonic ester 331
" " " Note on tribrommononitrobenzol 363
"Jahrbuch der Chemie," review 480
Jones, A. Analysis of electric calamine from Wythe County, Va. 621
Jones, H. C. See *Morse, H. N.*

KALE and turnip salad and okra, analyses 625
Kastle, J. H. The decomposition of silver chloracetate considered in the light of Ostwald's theory of affinity 586
Keiser, E. H. Composition of the explosive copper and silver compounds of acetylene 285
Keller, H. F., and *Smith, E. F.* The atomic weight of palladium 423
Kinney, W. J., *Wenger, W. H.*, and *Dunnington, F. P.* Analysis of washing powders 623
Kopp, Hermann. Obituary note 257
Kremers, E. On citronellone, an unsaturated fatty aldehyde 203
" " See *Sieker, F. A.*

"LABORATORY Practice" (*J. P. Cooke*), review 247
Layers, formation of in solutions of salts in mixtures of water and organic liquids 380
Lead, double halides of 107
"Lehrbuch der Technischen Chemie" (*H. Ost*), review 249

Lengfeld, F. The preparation of formic acid 259
Linebarger, C. E. Dissociation of salts into their ions by water of crystallisation 604
" On the application of the Friedel-Crafts reaction to syntheses in the anthracene series 602
" On the formation of layers in solutions of salts in mixtures of water and organic liquids 380
" On the preparation and constitution of para-anthracene 597
Lyons, R. E. See *Van Nüys, T. C.*

MAGNESIUM chloromanganite 149
" bromo-manganite 150
Maize kernel, proteids of 20
Manganese chloride and potassium chloride, compounds of 129
" double halides of 127
Manganous chloride 127
" " crystallography 128
"Manual of Chemistry" (*A. P. Luff*), review 551
Marble, statuary, from Rutland, Vt., analyses 626
Melville, W. H. See *Hillebrand, W. F.*
Menthene 291
Mercurous hypochlorsulphite, experiments with 182
Metabromchlorparaamidophenol 564
Metabromchlorparanitrophenol 563
Metabromchlorquinone, synthetic preparation of 563, 564
Metallic films, colors and absorption-spectra 185
Metals, colors and absorption-spectra of incandescent vapors of 185
"Methods of Gas Analysis" (*W. Hempel*), review of English translation 248
Meyer, V., and *Wachter, W.* Iodoso-benzoic acid 478
Michael, A. On the constitution of sodium acet-acetic ether 481
Michaud, G., and *Tristan, J. F.* Researches on the sugar of the *Agave Americana* 548
Mono-ammonium bromo-stannite 96
Mono-ammonium chloro-stannite 93
Mono-potassium-bromo-stannite 95
Mono-potassium-chloro-stannite 90
" " -bismuthite 168
Mono-rubidium chloro-bismuthite 176
Morse, H. N., and *Jones, H. C.* Redetermination of the atomic weight of cadmium 260
" *White, J. Jr.* Transportation of solids in a vacuum by the vapors of metals 314
Mond, L., and *Quincke.* Iron-carbon-monoxide 80

NEUBERG, O. The vapor-density of ammonium chloride 79
Newbury, S. B. On the copper sulphites 232
α_1-nitro-α_2-diazo-naphthalene nitrate, preparation and properties 53
" " " decomposition in alcohol 54
α_2-nitro-β_2-diazo-naphthalene nitrate, preparation and properties 53
" " " " preparation and properties 50
" " " " decomposition in alcohol 51
β_2-nitro-α_2-diazo-naphthalene sulphate, preparation and properties 47
" " " decomposition in alcohol 49
Nitrogen, stereochemistry of 316
Nitronaphthylamines, decomposition of the diazo compounds obtained from, with alcohol 45
Nitroso-phenol, ethers of 276
Noelting, E., and *Grandmougin, E.* The preparation of hydrazoic acid 78
Notes 76, 252, 329, 477
Noyes, W. A. Dibenzylcarbinamine and its conduct towards nitrous acid 225

OAT KERNEL, proteids or albuminoids of 212
" crystallised proteid of 682
Obituary notes 254, 257, 258, 259, 329, 477
Okra and kale and turnip salad, analyses 625
Orndorff, W. R., and *Cauffman, M.* Decomposition with alcohol of the diazo compounds obtained from some of the nitro-naphthylamines 45
Ortho-aldehydo-salicylic acid 299
Ortho-hydroxy-aldehydes, action of acetyl chloride on 293
Ortho-nitro-salicylic aldehyde 297
Osborne, T. B. Crystallised vegetable proteids 662
" Proteids of the flax-seed 629
" Proteids or albuminoids of the oat kernel 212
" See *Chittenden, R. H.*
"Outlines of Theoretical Chemistry" (*Lothar Meyer*), review 246
Oxalacetic ether hydrazide, condensation products of 576

PALLADIUM and platinum, electrolytic separation from iridium 435
Palladium, atomic weight 423
Pallado-diammonium chloride, preparation 424
Palmer, A. W. Note upon the reduction of symmetrical triamido-trinitro benzene 377
Para-anthracene, preparation and constitution of 597
Parabromchloraniline hydrochloride 562
" " sulphate 562
Parabromchlorquinone, synthetic preparation of 561, 562
Para-chlor-salicylic aldehyde 295
Para-methyl-salicylic aldehyde 298
Para-nitro-salicylic aldehyde 296
Paranthite from Clay County, North Carolina, analyses 628
Pentose carbohydrates, digestibility 9
Phenyl(5)ethoxypyrazol 583
" " " (3)carboxylate and salts 581, 582
Phenyl(3)methyl(5)ethoxypyrazol 584
Phosphorus oxychloride, action on aromatic silicic ethers 545
Pipette, improved, for gas absorptions 231
Platinum and palladium, electrolytic separation from iridium 435
Potassium antimony alum 171
" bismuth " 170
Potassium bromide and stannous bromide, compounds of 95
" bromoplumbite 124
Potassium chloride and stannous chloride, compounds of 89
" " " " bromide, compounds of 96
" chloromanganite 129
" " crystallography 133
" chloroplumbite 125
Potassium iodoplumbite 110
Prescott, A. B. The iodomercurates of organic bases 606
"Principles of Chemistry" (*D. Mendeléeff*), review of the English translation 251
"Principles of Theoretical Chemistry" (*I. Remsen*), review 552
Proteids of the corn or maize kernel 20
" of the flax-seed 629
" or albuminoids of the oat kernel 212
" vegetable, crystallised 662
Propionyl-malonic ether, properties 512
Pyrazolones, new method of converting acet-acetic ether and its derivatives into 516

QUINHYDRONES 574
Quinone, decomposition of the halogen addition products by heating in solution 560
Quinone dichloride 556
" " dibromide 559

Quinone tetrachloride 557
Quinone-oxime, ethers of 276
Quinones, action of haloid acids on 570
" preparation 555
Quincke. See *Mond, L.*

REMSEN, I. Researches on the double halides 81
Reviews and reports 58, 238, 316, 399, 550
Richardson, G. M. On the double halides of tin 89
Rubidium and bismuth chloride, complex 174
" chloro-antimonite 155
" chloro-manganite 142
" " crystallography 142

SALICYLIC ETHER, some reactions with 407
Salts, dissociation into ions by water of crystallisation 604
Saunders, C. E. On some double halides of antimony 152
" " " " " " " " manganese 127
Schorlemmer, C. Obituary note 477
"Scientific Correspondence of Joseph Priestley" (*H. C. Bolton*), review . . . 551
Shamel, C. H. Eupatorin: the active principle of *eupatorium perfoliatum* . . 224
Sicker, F. A., and *Kremers, E.* Menthene 291
Silicic ethers, catalytic action of aluminium chloride on 438
" " aromatic, action of phosphorus oxychloride on 545
Silver and copper compounds of acetylene, explosive 285
Silver chloracetate, decomposition considered in the light of Ostwald's theory of affinity 586
Silver chloracetate, rate of decomposition 587
Smith, E. F. The electrolytic separation of palladium and platinum from iridium . 435
" " " See *Keller, H. F.*
Sodium acet-acetic ether, constitution of 481
" " " behavior of carbon dioxide towards 501
" ethyl-malonic ether, action of acetylchloride on 503
" iodoplumbite 122
" malonic ether, action of acetylchloride on 495
" " " action of chlorcarbonic ether on 498
" " " behavior of carbon dioxide towards 501
" salicylic ether 411
" " " action of ethyl and methyl iodides on 415
" ethyl acet-acetic ether, action of chlorcarbonic ether on 506
" acet-succinic ether, action of phenyl hydrazine on 513
Squash-seed, crystallised proteid of 683
Stannous bromide and ammonium bromide, compounds of 96
" " " potassium bromide, compounds of 95
" " " " chloride, compounds of 96
" chloride, action on sodium chloride and lithium chloride 95
" " and ammonium chloride, compounds of 93
" " " potassium chloride, compounds of 89
Stas, Jean Servais. Obituary note 254
Stereochemistry 58, 316
Stokes, H. N. On the catalytic action of aluminium chloride on silicic ethers . . 438
" " " On the action of phosphorus oxychloride on aromatic silicic ethers . 545
" " " Note on benzene silicate 547
Stone, W. E. Digestibility of the pentose carbohydrates 9
Sugar of the *Agave Americana*, researches on 548
Sugars, configuration o 399
Sulphon-fluoresceïn 455
Sulphon-phthaleïns, investigations on 455

TAUTOMERISM 328
Tetra-ethyl silicate 452
Thorium and uranous sulphates, isomorphism and composition of 1
Tin, double halides of 89
Tinsley, J. D. Analyses of kale and turnip salad and okra 625
Toluquinone, action of hydrochloric acid on 573
" additive products 553, 565
" decomposition products 568
" dibromide 566
" dichloride 567
" preparation 565
Transportation of solids in a vacuum by the vapors of metals 31
Triamido-trinitro-benzene, reduction of symmetrical 377
Tribrommononitrobenzol, note on 363
" " action of sodic ethylate on 364
Tribromtrinitrobenzol, preparation 335
Tri-caesium chloro-bismuthite 181
Trimethylzanthine and some of its derivatives 611
Trinitrophenylene dimalonic ester, nitrite of 356
Trirubidium chloro-bismuthite 172
Tristan, J. F. See *Michaud, G.*
Tschernozem or black soil, analyses 621
Turnip and kale salad and okra, analysis 625

URANINITE 1
Uranous and thorium sulphates, isomorphism and composition of 1
Urine, carbon dioxide in 14

VAN NÜYS, T. C., and Lyons, R. E. Carbon dioxide in the urine 14
Vegetable proteids, crystallised 662
Volume lag and its bearing on molecular constitution 191

WACHTER, W. See *Meyer, V.*
Walker, C. Condensation products of acetacetic ether hydrazide and oxalacetic ether hydrazide 576
Washing powders, analysis 623
Waters, natural, new color standard for 300
Wenger, W. H. Solubility of cream of tartar in diluted alcohol 624
" " See *Kinney, W. J.*
Whitlock, T. C. See *Dunnington, F. P.*
White, J. Jr. See *Morse, H. N.*
Williams, G. H. Crystals of metallic cadmium 273
Wislicenus, W. The preparation of hydrazoic acid 479

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